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PREFACE TO THE THIRD EDITION

The aim in writing this text was to place before the students the fundamental principles of the subject with clarity and simplicity and yet in a sound and thorough manner. The same objective was kept in mind in subsequent editions too. In this edition, some major changes in the deduction of a number of formulae have been introduced in several chapters. A number of new problems to illustrate more clearly some physico-chemical phenomena in their application have been added. Physical Chemistry is not merely a collection of physical constants or a catalogue of derived mathematical formulations. Its main purpose is to interpret the nature of material changes in both qualitative and quantitative manner with special reference to the molecules and their structure. As before, efforts have been made to explain the physical meaning of the mathematical formulae with apt examples of their application so that the interpretation of the equations may be followed inductively. I believe this edition will continue to prove useful to the students and interesting to the teachers. I must express here my deep appreciation to the colleagues and teachers of chemistry who were kind enough to make helpful criticism and suggestion for the improvement of the book. I must take the responsibility of any error which might have crept in inspite of precautions.

Calcutta
March, 1973

P. C. R.

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THE GASEOUS STATE : THE KINETIC THEORY

Introduction. In chemistry, we deal with different kinds of matter, their changes and their interactions. In its study, as in all other sciences, we perform experiments, make observations and collect the data. We then proceed to interpret those data in order to understand the behaviour of the matter under investigation. Physical chemistry is primarily concerned with the interpretation of the observed facts connected with matter and its changes. In other words, physical chemistry has to develop and also to test the theories required to elucidate the results of the observations. It is a common knowledge with a chemist or a manufacturer that nitrogen and hydrogen would combine to form ammonia in presence of a catalyst under high pressure. It would be the business of a physical chemist to explain why high pressure and a catalyst are required. The object of physical chemistry would be not only to specify the properties of different states of matter and generalise them into laws but also to give a theoretical foundation to those generalisations. The purpose does not end here by simply suggesting a theoretical explanation of the experimental variables, it further predicts phenomena and their effects yet unknown. In doing these with precision, it has to take recourse to the generous application of the laws of physics and of mathematics. Evidently, the study of the influence of the physical factors like pressure, temperature, concentration, electric field, etc., on a substance or on a reaction is of importance in physical chemistry. Physical chemistry thus covers the ill-defined territory between physics and chemistry. But at the same time, it deals the chemical phenomena quantitatively by the use of mathematical machinery and the effects are given in a compactly condensed form. In order to express the theories quantitatively, the need of the detailed knowledge of the behaviour of the matter as a whole as also that of the atoms, molecules, ions, etc., are essential. Physical chemistry necessarily includes such studies.

The physical chemist has to carry out accurate determination of data in the laboratory and at the same time he has to philosophise the theory to explain his findings. That is, he is to exercise both his hand and his mind. He must know how to arrange for an apparatus for the resolution of the Raman spectra in the laboratory and also he must realise that the angular momentum during the orbital motion of an electron must be an integral multiple of $h/2\pi$.

The study of the physico-chemical problems is made basically from two essentially different directions. In one case, the structure of the matter—its constituent atoms and molecules—is presupposed and the behaviour of the whole matter or its change is interpreted on the basis of this atomic theory. This is what is called the *kinetic theory* approach. This is particularly helpful in finding out the speed or the progress of a process and also the mechanism of the same. The other approach is a *thermodynamic* one in which the structure of the matter is ignored. In this, our experience of the energy-changes and of their interconversion during a physical or a chemical process often help us in clarifying the cause of a reaction or the behaviour of a material system. We shall see later that with the help of the thermodynamic postulates it would be possible to arrive at valuable deductions. In this method we can predict the possibility of a phenomenon and can easily determine the extent of a reaction. The two modes of approach will be illustrated in various stages in the text.

It should be borne in mind that the quantitative aspects of the whole of chemistry have to be dealt with in Physical Chemistry. Thus, from experiments in the organic laboratory, we may find out the characteristic behaviour of methyl alcohol (CH_3OH) and establish the existence of the methyl or the hydroxyl group. But physical chemistry would give quantitatively the polarisation and the dipole moment of the molecule, the angle at which the different bonds are

linked, the interatomic distances, the dissociation energies of the bonds, etc. Thus, a complete knowledge of the substance will be available which would in their turn explain the behaviour of the substance.

In order to obtain a concept of the magnitude of a physical entity, it is necessary to choose some unit to measure the same. Each physical quantity requires its own unit. For this purpose, it had been possible to start with three basic standard units for mass, length and time. The units for these three are called fundamental units. The units of other physical quantities can be expressed in terms of the fundamental units and are called 'derived' units. The measure of the fundamental units and the expressions of the derived units are discussed briefly in *appendix 1.1*.

In this text, we shall deal in the beginning with the two essential principles—the kinetic theory and the thermodynamics—and the properties of matter in different states of aggregation, gases, liquids and solids. We shall subsequently consider the changes of matter under different conditions and under influence of different forces as also the changes of energy involved therein.

A. GASES : THE BEHAVIOUR OF GASES

1.1. The Gaseous State. Generally speaking, matter exists in three different states—solid, liquid and gaseous. The *solids* have definite shape and definite volume. Considerable force is however necessary to change either the volume or the shape. The *liquids* have definite volume but no definite shape. They take the shape of the vessel in which they are kept. No force is necessary to change their shape but force has to be exercised to compress them. The *gases* are characterised by the lack of definite volume or shape. In the gaseous state, the matter has the property of filling completely any available space to a uniform density. Low density and high compressibility are also pronounced characteristics of the gases.

The behaviour of gases is often quite simple and many physical properties are found to be identical for all gases, so that some simple rule would state the behaviour of all gases. The properties of liquids and solids differ widely from substance to substance and have to be studied individually. To illustrate such behaviour of the gases, we may consider the physical properties like compressibility or thermal expansion. For example, the volume of any gas is approximately halved when the pressure over the same is doubled. That is, all gases have the same compressibility. This is not so in the case of solids or liquids. Ether and water have different coefficients of compressibility. Again, all gases are found to expand to a similar extent when heated through the same interval of temperature (at const. pressure). All gases have approximately the same coefficient of expansion.

1.2. The Gas Laws. The identity in behaviour of different gases is evident from the fact that all gases generally obey some simple and common relations which are called the gas laws. These laws may be expressed in the following way.

(a) *Avogadro's Law.* The volume (v) of a gas depends not only upon the quantity of the gas (n) but also on its pressure (P) and its temperature (T).

It is common knowledge that at any given temperature and pressure, the volume of a gas will be directly proportional to the quantity. That is,

$$v \propto n \quad \text{when } P \text{ and } T \text{ are constant.}$$

$$\text{or} \quad v = k_1 n$$

The quantity n is usually expressed in gm-moles. So that if w gms of the gas of mol. wt. M be taken, then $n = \frac{w}{M}$ (I.1)

Avogadro (1811) was responsible for discovering a law of nature for the gases (commonly called *Avogadro's Law*) which states :

"Measured at a common temperature and pressure, the volumes of the same number of gram-moles of different gases, would be the same." That is, at the same temperature and pressure, the volume of n gm-moles of any gas will be the same.

Since $v = k_1 n$, when n is fixed, k_1 will be a universal constant, true for all gases.

(b) *Boyle's Law*. The volume of a given quantity of gas, at a constant temperature, is large at low pressure and small at high pressure. In 1662 Robert Boyle measured carefully the variation of the volume of a gas with pressure and established the relation which is known as the Boyle's Law. The law may be stated as, "At a constant temperature the volume of a given mass of gas varies inversely as its pressure." That is,

$$v \propto \frac{1}{P}, \text{ when } n \text{ and } T \text{ are constant,}$$

or

$$Pv = k_2 \text{ (constant)}$$

... (I.2)

The relation between pressure and volume can then be represented by a rectangular hyperbola as shown in Fig. I.1. As the value of the constant in equation (I.2) will change with temperature, there will be a separate curve for each fixed temperature. These curves plotted at different fixed temperatures are called *isotherms*.

(c) *Gay-Lussac's or Charles' Law*. The influence of variation of temperature on the volume of a gas was investigated by Gay Lussac (1802) and also by Charles (1787) independently. The quantitative relation derived from their experiments known as Gay-Lussac's Law or Charles' Law may be stated as,

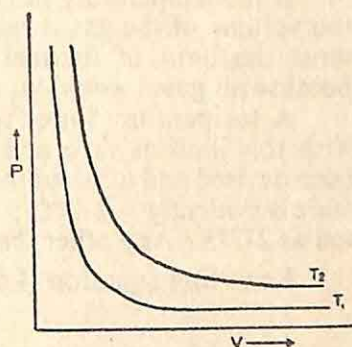


Fig. I.1. Isotherms ($T_2 > T_1$)

"At constant pressure, the volume of a given mass of gas expands by a constant fraction of its volume at 0°C for 1° degree rise in temperature."

If v_0 be the volume at 0°C and v at $t^\circ\text{C}$ of a given mass of gas at a constant pressure (P), then

$$v - v_0 = \alpha v_0 t$$

or

$$v = v_0 (1 + \alpha t)$$

... (I.3)

where α is the coefficient of expansion.

Unlike that in solids or liquids, the value of α is approximately the same for all gases. The magnitude is determined by measuring the volumes of the gas at 0°C and at 100°C , so that, from equation (I.3),

$$\alpha = \frac{v_{100} - v_0}{100v_0}$$

At higher pressures, the value of α varies to some extent, but if the pressure be kept constant and very low, the values tend to become identical for all gases. So, by extrapolating the experimentally determined values to zero pressure (Fig. I.2) the most accurate value has been obtained as

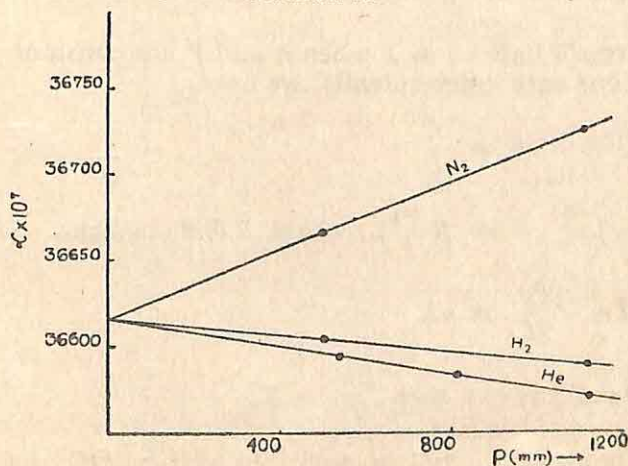


Fig. I.2. Determination of the accurate value of α

$$\alpha = 0.0036609 = \frac{1}{273.16} \approx \frac{1}{273} \quad \dots (I.4)$$

We can express now the volumes of a given quantity of gas at $t_1^\circ\text{C}$ and $t_2^\circ\text{C}$ (at const. pressure) as

$$v_1 = v_0 \left(1 + \frac{t_1}{273} \right) \quad \text{and} \quad v_2 = v_0 \left(1 + \frac{t_2}{273} \right)$$

$$\text{i.e.} \quad \frac{v_1}{v_2} = \frac{273+t_1}{273+t_2} \quad \dots (I.5)$$

If the temperature of the gas be lowered to -273°C , then, from equation (I.3), the volume of the gas is reduced to zero. In other words, this temperature represents the limit of thermal contraction of the gas. This is indeed hypothetical because all gases would liquefy or solidify before reaching this limit.

A temperature lower than this is inconceivable. A new scale of temperature with this limit as zero and having each degree equal to a centigrade degree has been devised and is called the *absolute scale of temperature*. The zero of the absolute scale is evidently -273°C ; and 0°C will correspond to 273°Absolute , often expressed as 273°K . Any other temperature, say $t^\circ\text{C}$, will be $(273+t)^\circ\text{K}$.

Rewriting equation (I.5), we have

$$\frac{v_1}{v_2} = \frac{273+t_1}{273+t_2} = \frac{T_1}{T_2}$$

where T_1 and T_2 are the temperatures in the absolute scale.

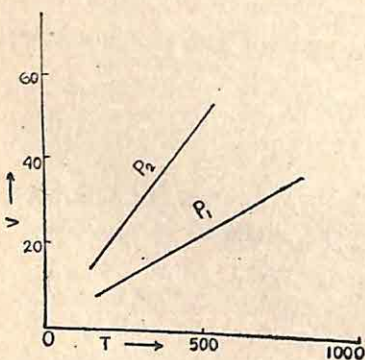


Fig. I.3. Isobars ($P_1 > P_2$)

The Charles' Law may be restated now :
"The volume of a given mass of gas at constant pressure is directly proportional to its absolute temperature." Hence

$$v = k_3 T, \text{ (when } n \text{ and } P \text{ are constant) (I.6)}$$

When volumes are plotted against absolute temperatures (at const. pressure) straight lines, called *isobars*, are obtained which on extrapolation converge to zero volume (Fig. I.3).

(d) *The Equation of State.* The gas laws discussed above may now be summarised :

(i) Avogadro's Law : $v \propto n$, when P and T are constant.

(ii) Boyle's Law : $v \propto \frac{1}{P}$, when n and T are constant.

(iii) Gay Lussac's Law : $v \propto T$ when n and P are constant. In other words, when all the functions vary independently, we have,

$$v \propto \frac{nT}{P}$$

or

$$v = R \frac{nT}{P}, \text{ where } R \text{ is a constant.}$$

$$\text{i.e.,} \quad \frac{Pv}{T} = nR \quad \dots (I.7)$$

For 1 gm-mole of any gas, then $\frac{PV}{T} = R$

$$\dots (I.8)$$

At any given temperature and pressure, the volume (V) of a gm-mole of any gas will be the same, i.e., ' R ' is a universal constant.

The equation (I.7) gives us a relation between the temperature, pressure and volume of a gas. Such a relation connecting P - v - T of a system is called an "equation of state." From this equation, it is obvious that for a given quantity of gas, any variation of pressure and temperature will be associated with such alteration in volume that the quantity Pv/T remains constant.

(i) Again, if the volume of a given mass of gas be kept constant (i.e., if n and v are constant), then

$$P = \frac{nR}{v} T = k'T \quad \dots (I.9)$$

or the pressure is directly proportional to the absolute temperature of the gas.

This has also been found true experimentally and formed another Law of Gay-Lussac. If pressures be plotted against absolute temperatures (volume being kept constant) linear graphs, called *isochores*, will be obtained (Fig. I.4).

(ii) There is another interesting deduction from this relation. If P_0 be the pressure of a gas at 0°C , then its pressure P_1 at another temperature $t_1^\circ\text{C}$ may be expressed by the relation,

$$P_1 = P_0(1 + a't_1) \quad \dots (I.10)$$

where a' is the coefficient of pressure change (at constant volume).

$$\text{Similarly,} \quad P_2 = P_0(1 + a't_2)$$

$$\text{Therefore,} \quad \frac{P_1}{P_2} = \frac{1 + a't_1}{1 + a't_2}$$

$$\text{But from (I.9),} \quad \frac{P_1}{P_2} = \frac{T_1}{T_2}; \quad \text{i.e.,} \quad \frac{1 + a't_1}{1 + a't_2} = \frac{T_1}{T_2} \quad \dots (I.11)$$

$$\text{From equation (I.3) and (I.6);} \quad \frac{1 + at_1}{1 + at_2} = \frac{v_1}{v_2} = \frac{T_1}{T_2},$$

where a is the coefficient of volume change.

Thus, we have, $a = a'$

Hence, the coefficient of pressure-change with temperature is the same as the coefficient of volume-change with temperature i.e., $1/273$. This has also been experimentally realised.

(iii) Since $Pv = nRT$, at a constant temperature for a given mass of gas, the volume will alter with increase or decrease of pressure in such a way that Pv

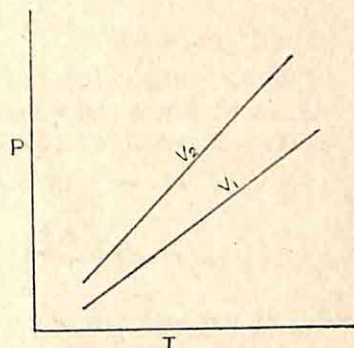


Fig. I.4. Isochores ($v_1 > v_2$)

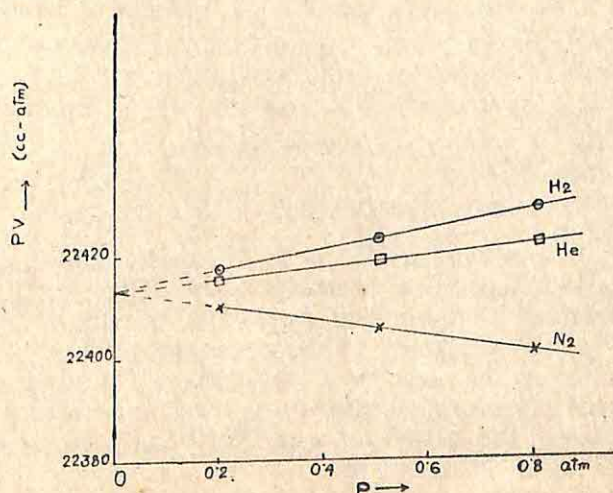


Fig. I.5. The volume of a gm-mole of gas at N.T.P.

shall remain constant. Though there are slight variations at high pressures, all gases tend to obey this relation at very low pressures. Thus, if we measure at constant temperature 0°C the volumes of 1 gm-mole of different gases at different pressures and plot the PV -values against P , we get the lines as in Fig. I.5. Extrapolation of these lines to $P = 0$ shows that all of them converge on the PV -axis, at a point $PV = 22.414$ litre-atmospheres. So, at 1 atmosphere and 0°C (or 273.16°K) the volume of a gm-mole of any gas is 22.414 litres.

(iv) *Value of the gas constant 'R'.* The general equation of state of n gm-moles of any gas is given by

$$Pv = nRT, \text{ i.e., } Pv = \frac{w}{M} RT \quad \left(\text{since } n = \frac{w}{M} \right)$$

For 1 gm-mole, $PV = RT$

V denotes the volume of a gm-mole.

Since we know the volume of a gm-mole of gas at standard temperature and pressure, it is possible to evaluate the gas constant, R .

$P = 1$ atmosphere, $T = 273^{\circ}\text{K}$, $V = 22.414$ litres.

$$\therefore R = \frac{P \times V}{T} = \frac{1(\text{atm}) \times 22.414 (\text{litres})}{273} = 0.082 \text{ litre-atmospheres}$$

per degree per mole. In c.g.s. units,

$$R = \frac{P \times V}{T} = \frac{76 \times 13.595 \times 981 (\text{dynes-cm}^{-2}) \times 22414 (\text{cm}^3)}{273}$$

$$= 8.314 \times 10^7 \text{ ergs per degree per mole.}$$

Since 1 calorie $\equiv 4.184 \times 10^7$ ergs

$$\therefore R = \frac{8.314 \times 10^7}{4.184 \times 10^7} = 1.987 \text{ calories per degree per mole.}$$

For ordinary calculations, the value of R may be taken as equivalent to (approximately) 2 calories per degree per mole. Evidently, R has the dimensions of energy.

Problem: Calculate the pressure exerted on the walls of a 3-litre flask when 7 gms of Nitrogen are introduced into the same at 27°C .

$$\begin{aligned} \text{We have } P &= \frac{w}{M} \cdot \frac{RT}{v} && (\text{mol. wt. of } \text{N}_2 = 28) \\ &= \frac{7}{28} \times \frac{0.082 \times (273 + 27)}{3} = 2.05 \text{ atmospheres.} \end{aligned}$$

(R used is in litre-atmosphere and the volume in litres.)

Problem: What is the molecular weight of a gas, 12.8 gms of which occupy 10 litres at a pressure of 750 mm and at 27°C ?

$$Pv = \frac{w}{M} \cdot RT$$

$$\text{or } M = \frac{w}{Pv} \cdot RT = \frac{12.8 \times 0.082 \times (273 + 27)}{\frac{750}{760} \times 10} = 31.84$$

(e) *Dalton's Law of Partial Pressures.* If a vessel contains a mixture of two or more gases, then the individual pressures of the different gases will depend upon the relative proportions of the constituents. The individual pressures are usually expressed as the partial pressures of the constituents. The partial pressure of a constituent is defined as the pressure it would exert if it alone occupied the entire volume of the vessel at the same temperature. Dalton studied the relation between the partial pressures of the constituents and the total pressure of the mixture and stated his law of Partial Pressures, as

"The total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases (at the same temperature)."

Thus, if a mixture of gases (temp. T) contains $n_a, n_b, n_c, \dots$ moles of different gases whose partial pressures are $p_a, p_b, p_c, \dots$ etc. respectively, the total pressure P of the mixture will be given by

$$P = p_a + p_b + p_c + \dots \quad \dots (I.12)$$

Applying the equation of state which is independent of the nature of the gases, we have

$$P = \frac{n}{v}RT \quad \dots (I.13)$$

where v is the total volume of the system, and n = total number of moles = $n_a + n_b + n_c + \dots$

Again, the partial pressures are

$$p_a = \frac{n_a}{v}RT, \quad p_b = \frac{n_b}{v}RT, \quad p_c = \frac{n_c}{v}RT, \quad \dots (I.14)$$

$$\text{Hence, } p_a + p_b + p_c + \dots = \frac{RT}{v} (n_a + n_b + n_c + \dots) = \frac{n}{v}RT$$

Therefore, $P = p_a + p_b + p_c + \dots$

Further, from equations (I.13 and I.14), we have

$$p_a = \frac{n_a}{n}P, \quad p_b = \frac{n_b}{n}P, \quad p_c = \frac{n_c}{n}P, \text{ etc.}$$

The partial pressure of a constituent can then be evaluated from the knowledge of the total pressure of the mixture and the relative proportion of the constituents.

Problem : 400 gms of Hydrogen mixed with 1400 gms of Nitrogen are kept at a pressure of 200 atmospheres. What are their partial pressures?

$$\text{Gm-moles of hydrogen} = \frac{400}{2} = 200, \quad \text{gm-moles of nitrogen} = \frac{1400}{28} = 50.$$

$$\text{Total No. of moles} = 200 + 50 = 250$$

$$\therefore p_{H_2} = \frac{200}{250} \times 200 = 160 \text{ atm.} \quad p_{N_2} = \frac{50}{250} \times 200 = 40 \text{ atm.}$$

Problem : 20 c.c. of oxygen was collected over water at a pressure of 749 mm at 25°C. What will be the volume of the dry oxygen at N.T.P.? The vapour pressure of water at 25°C is 24 mm.

The partial pressure of oxygen in the dry state = $749 - 24 = 725$ mm.

$$\text{If } v \text{ be its volume in the dry state at N.T.P. then } \frac{760 \times v}{273} = \frac{725 \times 20}{298},$$

whence

$$v = 17.48 \text{ c.c.}$$

(f) **Law of Partial Volumes (Amagat).** This law, which is really equivalent to the law of partial pressures, states that the *total volume* of a gas mixture is the sum of the partial volumes of the constituents of the mixture, i.e.,

$$V = v_1 + v_2 + v_3 + \dots$$

where V is the total volume and $v_1, v_2, v_3, \dots$ are the partial volumes of the constituents. The partial volume of a constituent is defined as the volume which the particular constituent would occupy at the total pressure of the mixture, the temperature always remaining constant.

From the gas equation we have,

$$v_1 = \frac{n_1}{P}RT; \quad v_2 = \frac{n_2}{P}RT, \text{ etc.}$$

$$\text{i.e., } v_1 + v_2 + v_3 + \dots = \frac{RT}{P} (n_1 + n_2 + n_3 + \dots) = \frac{nRT}{P} = V$$

$$\text{Moreover, } v_1 = \frac{n_1}{n}V, \quad v_2 = \frac{n_2}{n}V, \quad \text{and so on}$$

(g) *Graham's Law of Effusion.* The passing out of a gas through a fine orifice made in the wall of the container is called effusion. The rate of effusion, i.e., the volume of the gas passing out, depends on the density of the gas, the pressure and the temperature. The quantitative relation governing such effusion was first found by Graham (1829). This law is enunciated as,

"At constant temperature and pressure, the rates of effusion of different gases vary inversely as the square root of their densities."

If a gas passes out through a porous wall, say of unglazed earthenware or compressed graphite, etc., the process is called *diffusion*. The same law, as stated above, would be applicable in the case of diffusion.

If r_1 and r_2 be the rates of effusion (or diffusion) of two gases having densities d_1 and d_2 , (T and P constant), then

$$r_1 = \frac{k}{\sqrt{d_1}} \quad \text{and} \quad r_2 = \frac{k}{\sqrt{d_2}}$$

or

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \quad \dots (I.15)$$

i.e.,

$$r\sqrt{d} = \text{constant.}$$

This is established from the results recorded below.

EXPERIMENTAL RESULTS ON THE GRAHAM'S LAW OF DIFFUSION

Gas	Density	Velocity of diffusion (Air = 1)	$r\sqrt{d}$
Hydrogen	0.0695	3.83	1.01
Oxygen	1.1056	0.9487	1.00
Nitrogen	0.9712	1.0144	1.00
Carbon dioxide	1.530	0.8122	1.04
Methane	0.559	1.344	1.00

Let t_1 and t_2 be the time required for the passage of the same volume v of the two gases through the same hole.

$$\frac{v}{t_1} = r_1 \quad \text{and} \quad \frac{v}{t_2} = r_2$$

$$\therefore \frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} \quad \dots (I.16)$$

Since temperature and pressure are fixed, the molar volume v_m of both the gases must be the same. We have, thus,

$$\frac{t_2}{t_1} = \sqrt{\frac{d_2 v_m}{d_1 v_m}} = \sqrt{\frac{M_2}{M_1}} \quad \dots (I.17)$$

where M_1 and M_2 are the respective mol. wts.

This relation enables us to determine the mol. wt. of a gas by comparing the time of its effusion through a given orifice with that of a known gas. This is usually done in an effusimeter, one form of which is shown in Fig. I.6.

A known gas, (say oxygen) is taken over mercury in the bulb A upto a fixed mark y . The bulb is closed at the top by a three-way stop-cock. The exit is connected to the funnel B . Sealed into the funnel B is a thin metal sheet with a small perforation through which the gas can effuse out under the pressure of mercury in C . The time t_1 taken by the mercury to travel from y to x is noted. The experiment is repeated with the gas of unknown mol. wt. M_2 and the time t_2 is also noted

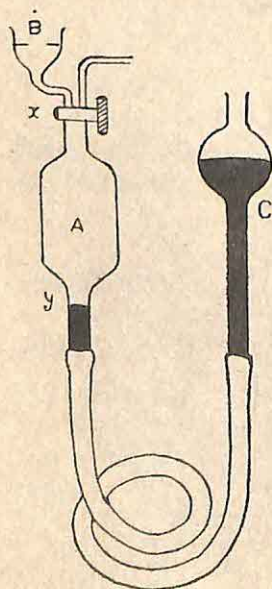


Fig. I.6. Effusimeter

Then, $\frac{t_1}{t_2} = \sqrt{\frac{32}{M_2}}$, from which M_2 is obtained. This has actually been utilised in determining the mol. wt. of ozone.

Problem : Ladenburg found that a sample of ozonised oxygen containing 86.16% of ozone by weight required 430 seconds to diffuse under conditions where pure oxygen required 367.5 seconds. Determine the vapour density of ozone.

Let v be the volume diffusing out in each case. Let d_m , d_o and d be the densities of the mixture, pure oxygen and ozone respectively.

$$\frac{v/430}{v/367.5} = \sqrt{\frac{d_o}{d_m}} = \sqrt{\frac{16}{d_m}}$$

or

$$d_m = \left(\frac{430}{367.5} \right)^2 \times 16 \approx 21.91$$

Again for 100 gms, the volume,

$$\frac{100}{d_m} = \frac{86.16}{d} + \frac{13.84}{d_o}$$

or

$$\frac{100}{21.91} = \frac{86.16}{d} + \frac{13.84}{16}$$

whence

$$d = 23.3$$

Another practical application of the Graham's law is in the partial separation of the components in a gas mixture. If the mixture is led through a tube made of porous walls, in a given time the lighter component will diffuse out more than the heavier one. By repeating the process with each separate fraction from diffusion, the concentration of one component can be considerably increased compared to that of the other. This is called *atmolysis*. Argon has been concentrated in nitrogen in this way. The isotopes of neon, chlorine etc. have been partially separated by this method.

I.3. Critical State. Gases are liquefied by lowering of temperature and increase of pressure. Of these two factors, the temperature plays a more important role. Most gases can be liquefied at ordinary pressure (1 atm.) by lowering the temperature considerably. But many gases like O_2 , H_2 , N_2 etc., at ordinary temperature cannot be liquefied however high the pressure may be. For every gas, there is a temperature above which liquefaction is impossible whatever may be the pressure. This limiting temperature above which liquefaction is impossible is called the *critical temperature* (T_c) of the substance. The minimum pressure necessary to bring about liquefaction of the gas at the critical temperature is called the *critical pressure* (P_c). The volume occupied by a gm-mole of the substance at the critical temperature and pressure is called the *critical volume* (V_c).

The idea of the critical state may be best explained from the classical experiments of Andrews (1861) on his researches on carbon dioxide. He studied the P - V relations of carbon dioxide at different constant temperatures. A broad outline of Andrews' apparatus is given in Fig. (I.7). In a very narrow glass tube AB, a quantity

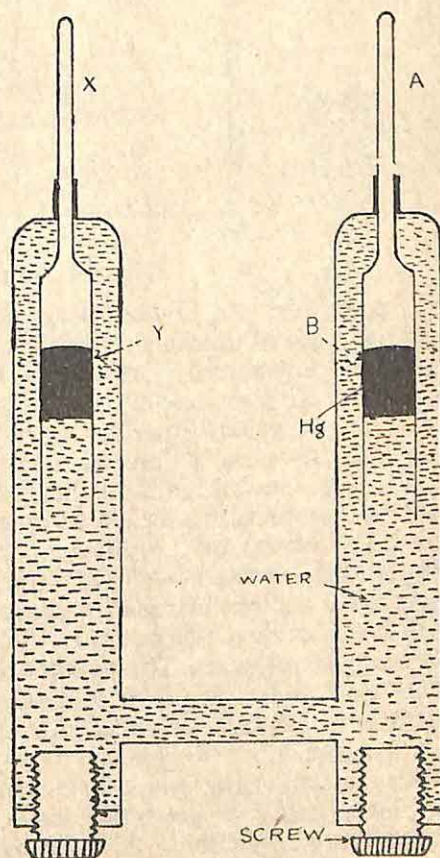


Fig. I.7. Andrews' apparatus

of gas (CO_2) was enclosed and sealed off by a small pellet of mercury. The glass tube is fitted into a strong copper tube containing water. Exactly a similar arrangement (XY) was also made in which air was used instead of CO_2 , and attached to the first. The second one served as a manometer from which the pressure was noted. The pressure (upto about 400 atm.) was exercised by screwing steel screws at the bottom. He found that no liquefaction of carbon dioxide occurred above 31.1°C . Below this temperature, liquid carbon dioxide is formed at definite pressure. This temperature (31.1°C) is the critical temperature of carbon dioxide.

The isothermals obtained by plotting graphically the P - V data of Andrews' experiments are shown in Fig. I.8. From Boyle's law ($PV = \text{constant}$) we expect that the isothermal will be a rectangular hyperbola. At higher temperatures, say 48°C , the isothermal is found to be hyperbolic, approximately obeying the Boyle's law. But as the temperature is lowered, the isothermals deviate increasingly from

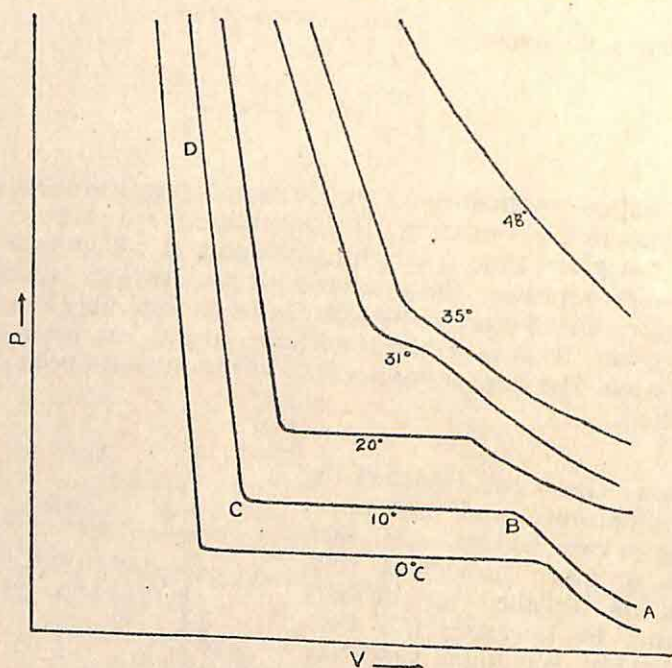


Fig. I.8. Isotherms of carbon dioxide

the hyperbolic. At low temperatures (say 10°C), the curve breaks into three parts. With increase of pressure, there is a decrease in volume of the gas along AB. Then there is a horizontal portion (BC) of the curve, showing considerable decrease in volume with practically no increase in pressure, indicating the occurrence of liquefaction. When liquefaction is complete (at C) the isothermal rises abruptly along CD showing volume-decrease of the liquid is very small for large increase in pressure. Such breaks in the isothermals at other low temperatures are found until the temperature 31.1°C is reached. The horizontal portions (where liquefaction takes place) of the different isothermals become smaller and smaller as the temperature is raised. At 31.1°C , the horizontal portion practically disappears, showing that for a slight increase in pressure there is an enormous shrinkage in volume. This is the critical temperature. The P - V curve at this temperature is referred as the critical isotherm. The substance is said to be in the critical state if it is kept at its critical temperature and its critical pressure. In the critical state, (i) the liquid and the gaseous states are indistinguishable, there is no surface of separation between the two phases, and (ii) the compressibility is very high. Below the critical temperature, the substances in the gaseous phase are called vapours, and the term 'gases' is generally used when the temperature is above the critical temperature. Faraday (1823) liquefied, by cooling and compression, many gases like chlorine, ammonia, hydrogen sulphide, hydrogen chloride, etc., but failed to liquefy oxygen, hydrogen, nitrogen, etc. These came to be known as 'permanent

gases.' The failure was due to the lack of the knowledge of the existence of the critical temperature above which liquids are non-existent. These so-called permanent gases have low critical temperatures, not attainable in those times.

Determination of the Critical Constants. (a) *Critical pressure and temperature.* A small quantity of the substance is enclosed over mercury in a closed bulb A, attached to the manometer B (Fig. I.9). The bulb is surrounded by a jacket, the temperature of which can be adjusted according to requirements. The surface between the liquid and the vapour is carefully observed. If necessary, the temperature is lowered to obtain a portion of the substance in the liquid state. Subsequently, the temperature is gradually raised until the meniscus just disappears. This temperature is recorded as its critical temperature and the critical pressure is obtained from the manometer-reading.

Cailletet used another device to determine these critical constants. A quantity of the liquid and its vapour were taken in a tube over mercury. By adjustment of the mercury level, the volume of the liquid-vapour system was kept constant. The pressure was measured from an attached manometer. It is known that the vapour pressure at any temperature would be independent of the mass of the liquid. When vapour pressures were measured at different temperatures with different masses of liquids, the P - T curves became identical. But beyond the critical temperature, since there was no liquid, the system was entirely gaseous, the P - T curves would be different with different masses of the substance. Cailletet actually found the vapour-pressure curve branching off at a certain point as shown in Fig. I.10. This point is independent of the mass of the liquid taken and naturally this would be the critical temperature of the substance. From the corresponding ordinate, the critical pressure was obtained. (Fig. I.10)

(b) *Determination of the critical volume.* With the rise in temperature, the density of a liquid decreases while the density of its saturated vapour increases. If these densities of liquid and saturated vapour be plotted against temperature, curves ABC and DEF are obtained as in Fig. I.11. It was discovered by Cailletet and Mathias that the mean of the densities of liquid and saturated vapour bears a linear relation to temperature. That is, when the mean of the points on ABC and DEF are plotted, a straight-line XY is obtained. This is commonly called the *law of Cailletet and Mathias*. If d_l and d_g denote the two densities, then

$$\frac{1}{2}(d_l + d_g) = a + bt$$

where a and b are constants.

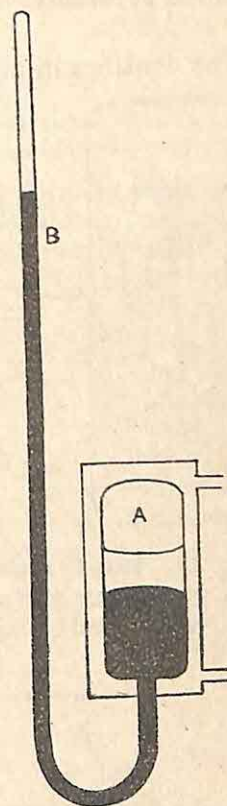


Fig. I.9. Det. of critical temp. and pressure

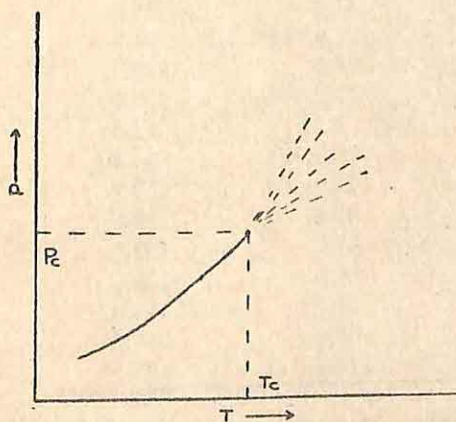


Fig. I.10. Vap.-press. curves to determine T_c (Cailletet)

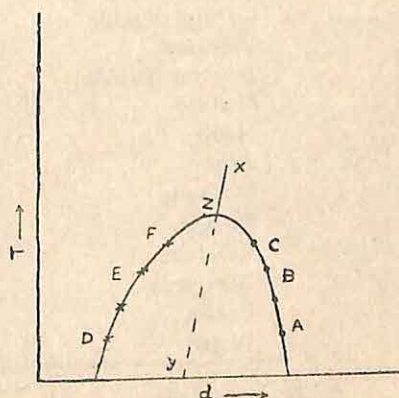


Fig. I.11

The two curves *ABC* and *DEF*, when extrapolated, cut at the point *Z* where obviously the densities of the liquid and its saturated vapour are identical. This would occur only at the critical temperature. The point *Z* then corresponds to the critical density and it should also lie on the line of mean densities, *xy*. The curves *ABC*, *DEF* are first drawn from experimental results (near the critical temperature) and the point *Z* is determined from extrapolation. The value of the critical density (d_c) is thus known, from which the critical volume is obtained, for $V_c = M/d_c$.

The experimental determination of the densities is carried out by enclosing a known quantity of the liquid in a graduated sealed tube and keeping it at a constant (known) temperature. The volumes of the liquid and the vapour are read off from the graduations. The experiment is repeated with another quantity of the substance at the same temperature. If ' ω ' and ' v ' denote masses and volumes of the substance, then

$$\omega = v_l d_l + v_g d_g \quad \text{and} \quad \omega' = v_l' d_l + v_g' d_g$$

The densities d_l and d_g are evaluated from these two relations.

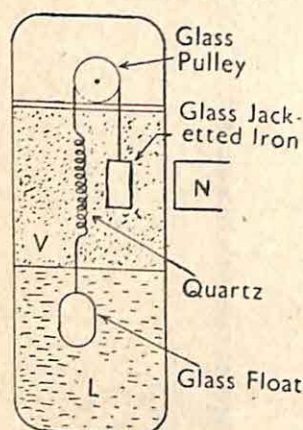


Fig. I.12. Maass's apparatus for measurement of densities of liquid and vapour

(ii) Maass devised a very ingenious method for the determination of the critical volume. His apparatus is a strong-walled small pyrex-glass tube containing the liquid and its vapour. A small glass float of known volume and mass was suspended inside by a calibrated quartz spiral. The suspension is balanced by a glass-jacketed iron counterweight over a pulley (Fig. I.12). The float can be raised or lowered by an external magnet. The whole apparatus is kept in a carefully-controlled thermostat. At every temperature the weight of the float is determined both in the liquid and in the vapour from the extension of the spring. The weights of the displaced vapour or liquid are calculated and from these the densities are obtained.

The critical constant values of some commonly used substances are given here.

CRITICAL CONSTANTS

Gas	Critical temperature °K	Critical pressure (atm.)	Critical volume (c.c.)
Oxygen	154.28	49.7	74.4
Hydrogen	33.2	12.8	69.7
Nitrogen	125.97	33.5	90.0
Ammonia	405.5	111.3	72.0
Carbon monoxide	133.0	34.5	90.0
Carbon dioxide	304.15	72.9	94.2
Chlorine	417.0	76.1	123.5
Sulphur dioxide	430.25	77.7	125.0
Helium	5.2	2.25	61.55
Neon	44.75	26.86	44.30
Argon	150.6	77.0	150.7
Methane	190.3	45.6	98.8
Ethane	305.4	48.0	142.8
Ethylene	283.0	50.6	126.0
Acetylene	308.6	61.7	113.0
Benzene	562.0	48.6	256.0
Water	647.3	218.5	55.54

Continuity of State. The transition of the gaseous state to the liquid state is not sudden and discontinuous as it may appear from the breaks in the isothermals

at temperatures below the critical temperature. In fact, the gas passes into the liquid state imperceptibly and continuously. This may be shown from the following considerations.

In Fig. I.13, y represents the isothermal of CO_2 at the critical temperature (31.1°C), and z is an isothermal below the critical temperature, say at 20°C . Let us start with CO_2 gas at the point A and gradually compress the gas. At the point B , liquid will begin to appear and all along BC (at const. pressure) the system would be a heterogeneous mixture and would apparently show discontinuity. At the point C , it would be entirely liquid which may be compressed to D , along the path CD .

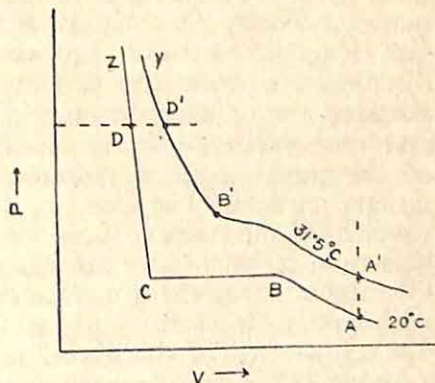


Fig. I.13. Isotherms of CO_2

Now, this transition may be effected in another way. The gas at A may be heated at constant volume until the temperature attained is the critical one (31.1°C) represented by A' . The gas may then be isothermally compressed to follow the path $A'B'$. At B' the critical point is reached, where the liquid and gas are indistinguishable. On slight rise of pressure, the gas is completely transformed into liquid which changes, along $B'D'$, to D' . The liquid at D' may now be cooled at constant pressure until the point D is reached. We have thus, by a new path, transformed the gas at A to the liquid at D as before without any heterogeneity at any point. The transition is nowhere abrupt and is a continuous one. This phenomenon is often termed as the continuity of state.

I.4. Coefficient of Expansion and Compressibility. (i) At a constant pressure, the volume of a gas increases with rise in temperature. The increment in volume per c.c. for unit rise in temperature, i.e., the coefficient of isobaric expansion is denoted by α , or

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \quad \dots (I.18)$$

Since $Pv = nRT$, we have $\left(\frac{\partial v}{\partial T} \right)_p = \frac{nR}{P}$

$$\therefore \alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{1}{v} \cdot \frac{nR}{P} = \frac{nR}{nRT} = \frac{1}{T} \quad \dots (I.19)$$

(ii) At a constant temperature, the volume of a gas decreases with rise in pressure. The coefficient of isothermal compressibility, i.e., decrement in volume per c.c. for unit rise in pressure, is denoted by β ,

$$\text{or } \beta = - \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \quad \dots (I.20)$$

The negative sign indicates the decrease in volume.

Since $Pv = nRT$, $\left(\frac{\partial v}{\partial P} \right)_T = - \frac{nRT}{P^2}$

$$\text{or } \beta = - \frac{1}{v} \left(\frac{-nRT}{P^2} \right) = + \frac{nRT}{nRT \cdot P} = \frac{1}{P} \quad \dots (I.21)$$

B. THE KINETIC THEORY OF GASES

I.5. The Kinetic Theory. In the preceding section we discussed the common behaviour of gases and the laws generally obeyed by them. These laws are derived

from experimental observations. For an explanation of such behaviour of gases, some theoretical foundation is essential. The abstract speculation in this direction must naturally begin with the ideas as to the nature and ultimate structure of the material world. As early as in 500 B.C. Leucippas and Democritus in Greece and Kanādā in India proposed the atomic theory stating that matter was discontinuous consisting of minute particles now called molecules and that these particles were always in motion. Not much progress was made until Gassendi, and later on Hooke, in the seventeenth century explained the physical phenomena of the gases on the assumption of the existence of rapidly moving independent minute particles. The credit of a systematic attempt to explain the properties of gases on a mechanical basis for the first time goes to Bernoulli (1738). It was also soon realised that heat was a manifestation of molecular motion. In a solid the minute particles (or molecules) are held very closely together and are entirely devoid of any translatory motion. If now thermal energy be imparted into the solid, it takes the form of vibrational and rotational motion along with some translatory movements. These are manifested as heat is added and the temperature rises. With further increase in the absorption of thermal energy, the energy of vibration rises to such an extent that the particles break away from the compact state and the solid is transformed into liquid. Further absorption of heat causes the particles to break away from the restraining forces holding them together and the particles move away freely from the liquid to the gaseous state. The gases then are essentially composed of freely-moving molecules. These basic ideas were at the root of the theory to explain the behaviour of gases called the *Kinetic Theory of Gases*. The present state of the theory developed as a result of the thoughts and contributions of not one but a host of great minds spread over centuries. In the nineteenth century especially, through the efforts of Joule, Kronig, Clausius, Boltzmann and Maxwell, the theory succeeded to attain a rigid mathematical form.

As in all theories, the kinetic theory of gases also begins with certain basic assumptions. The tenets of the theory may be summarised as follows :

(1) Gases are composed of minute discrete particles, now called molecules. In any one gas all the molecules are of the same size and mass, but these differ from gas to gas.

(2) (a) The molecules within a container are in ceaseless chaotic motion with high velocities, incessantly colliding with each other and with the walls of the container.

(b) In spite of the enormous number of collisions, the molecular density in any volume of the gas is not disturbed, i.e., the molecules at one place do not collect in larger number than at another. At each collision, however, the velocities are altered in direction and in magnitude.

(c) Between two collisions, a molecule moves in a straight line with uniform velocity. The period during which the collision lasts is negligible compared with the time to traverse the distance between two successive collisions, called the free path.

(3) The bombardment of the molecules on the walls of the container gives rise to the *pressure* of the gas. The average force per unit area which the molecules exert in their impacts with the walls per unit time is the pressure. The larger the number of impacts, the greater will be the pressure.

(4) The molecules are supposed to be perfectly *elastic*. In the collisions between one another or with the walls, no energy is lost.

(5) The dimensions of the molecules are negligible compared to the free paths they traverse, and at ordinary or low pressures, they are taken as point masses.

At relatively low pressures, because of the comparatively large distances between the molecules, the forces of attraction between the molecules are also negligible.

(6) The temperature of a gas is a measure of the average kinetic energy of the molecules of the gas in the system.

If the temperature is raised, the molecules would move more vigorously result-

ing in a larger number of impacts on the wall at a constant volume. That is why we find an increase of pressure with rise in temperature at constant volume.

On the other hand, if the volume is decreased at a constant temperature, the molecules would strike the walls more frequently and the pressure-increase would occur.

I.6. Evidence in Support of the Kinetic Theory. Direct evidence in support of the basic assumptions of the theory, *viz.*, existence of molecules and of their motion cannot be given but, though indirect, convincing proofs in this regard are obtained from the following :

(i) All gases diffuse readily into one another until these are homogeneously mixed. If we let loose a little chlorine gas near the floor of the room, the gas would diffuse on all sides and also to the ceiling against gravity. This is possible only if there are small particles which move in all directions.

(ii) The expansibility of a gas to an infinite extent is another evidence. A gas spreads immediately throughout any empty space in which it is placed. Obviously the gas must be composed of minute particles with motion. We have also seen how the increase in kinetic energy may lead to vaporisation.

(iii) The rectilinear motion of the gas molecules was first demonstrated experimentally by Dunoyer (1911) and subsequently by others. In this experiment a vertical cylindrical tube was taken. The tube was divided into three chambers by two partitions X and Y (Fig. I.14). Each partition had a small circular hole at the centre. In a small oven a little sodium was taken at the bottom of the lowest chamber, and the vessel was evacuated. On heating, sodium evaporated and the molecules escaped rapidly in all directions, most of them being deposited on the walls of the lowest chamber. Some of these will pass through the hole X. Out of these again some would pass through the hole Y and enter the topmost compartment making a deposit on the roof of the cylinder. The deposit was formed to coincide exactly with the projection of the hole Y. The experiment may be varied by removing partition Y and suspending a disc there, when a shadow is formed on the deposit on the roof. This not only shows that the molecules move in straight lines but also that there is no repulsive force between the molecules. Had there been repulsive forces, the molecules would deviate in the upper chambers and would not follow rectilinear paths.

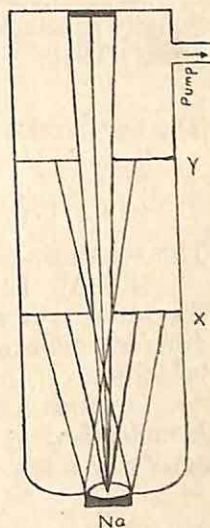


Fig. I.14. Dunoyer's Experiment

(iv) In 1827, the botanist Brown observed that pollen grains suspended in a liquid danced about wildly even when the temperature was maintained constant. The same phenomenon, called Brownian motion, is also observed when a colloidal suspension is examined under an ultramicroscope. The motion of the suspended particles is irregular, spontaneous and perpetual, and takes place in all kinds of media. This can be explained only if we assume that suspended particles are really pushed from different directions by the molecules of the media. In consequence unbalanced forces act on the particle and cause it to move about chaotically. We shall later on discuss, in more details, the character of the Brownian motion. Besides these, the derivation of the gas laws from the kinetic theory supports the latter.

I.7. Velocity of Gas Molecules. It would be useful to mention here some elementary considerations which are made in the computation of velocities of the gas molecules.

(i) Suppose a molecule has velocity c_1 and suppose x , y and z are its components along three axes perpendicular to one another. Then,

$$c_1^2 = x^2 + y^2 + z^2 \quad \dots (I.22)$$

(ii) In a given mass of gas, a large number of molecules would have the

same velocity c_1 in magnitude but in different directions. Evidently, the magnitudes of the components along any given axis, say x -axis, would be different. Let the component-velocities of the different molecules along x -axis be denoted by $x_1, x_2, x_3, \dots$ etc. Since all directions are equally possible, the components in the two opposite directions along x -axis must balance one another, i.e., mean value of the components, $\bar{x} = 0$. Similarly, along the other two axes, $\bar{y} = 0$ and $\bar{z} = 0$.

But the mean of the squares of these components will not be zero, for squares are all positive. That is, $\bar{x}^2 \neq 0$. This is also true along other two axes.

Now there is no preference for any particular direction, all directions being equally probable, the mean values of the squares along all the three axes must be equal. Then,

$$\bar{x}^2 = \bar{y}^2 = \bar{z}^2 \quad \dots (I.23)$$

The bar overhead indicates the mean values.

$$\text{So,} \quad c_1^2 = \bar{x}^2 + \bar{y}^2 + \bar{z}^2 = 3\bar{x}^2$$

$$\text{or} \quad \bar{x}^2 = \frac{1}{3}c_1^2 \quad \dots (I.24)$$

This relation would be generally true for all magnitudes of the velocity, c_1 .

(iii) All the molecules have not got the same velocity. Even if we start with the same velocity for all the molecules, very soon due to ceaseless collisions, different molecules would acquire different kinetic energies and hence different velocities.

Suppose a given quantity of gas contains N molecules. Out of these total N molecules, n_1 molecules with a velocity c_1 have each kinetic energy ϵ_1 , n_2 molecules with a velocity c_2 have each kinetic energy ϵ_2 , and so on. Then

$$N = n_1 + n_2 + n_3 + \dots$$

$$N\epsilon = n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + \dots$$

where ϵ is the kinetic energy possessed by a molecule on an average. We have, therefore, when m is the mass of a molecule,

$$N \times \frac{1}{2}m\bar{c}^2 = n_1 \times \frac{1}{2}mc_1^2 + n_2 \times \frac{1}{2}mc_2^2 + n_3 \times \frac{1}{2}mc_3^2 + \dots$$

where c is the velocity of each molecule on the supposition that each molecule has the same average kinetic energy.

$$\text{Simplifying} \quad \bar{c}^2 = \frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \dots}{N} \quad \dots (I.25)$$

Hence, $\bar{c}^2$ is the mean of the squares of the velocities of all the molecules and is called the *mean-square velocity*.

$$\text{So,} \quad c = \sqrt{\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \dots}{N}} \quad \dots (I.26)$$

or c is the root of the mean-square velocity and briefly termed *root-mean-square velocity*.

The arithmetic mean of the velocities, denoted by c_a is given by

$$c_a = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \dots}{N}$$

This is often mentioned as *average velocity* and is evidently different from the root-mean-square velocity, c . It should also be noted that the mean-square velocity ($\bar{c}^2$) is not the same as the square of the mean speed, $(c_a)^2$.

For example suppose there are five molecules having speeds, 3, 4, 5, 6 and 7 metres per second. Then,

$$\bar{c}^2 = \frac{3^2 + 4^2 + 5^2 + 6^2 + 7^2}{5} = 27 \text{ metres/sec.}$$

$$\text{and} \quad c_a^2 = \left(\frac{3+4+5+6+7}{5} \right)^2 = 25 \text{ metres/sec.}$$

It will be seen later that $c = 1.085 c_a$.

I.8. The pressure of a gas. The postulates of the kinetic theory enable us to calculate the pressure of a gas in terms of molecular quantities.

Let us consider a volume of gas contained in a cubical box of side l . Let the number of molecules present in it be N , the mass of each molecule being m .

The molecules are moving constantly with different velocities in different directions bombarding on the walls of the cube. Consider any one molecule and suppose its velocity is c_1 at a given instant. The velocity c_1 may be resolved into three rectangular components x_1 , y_1 and z_1 along the axes parallel to the three edges of the cubical box. Then

$$c_1^2 = x_1^2 + y_1^2 + z_1^2$$

Now consider the motion of this molecule along x -axis perpendicular to the walls G and H of the vessel (Fig. I.15).

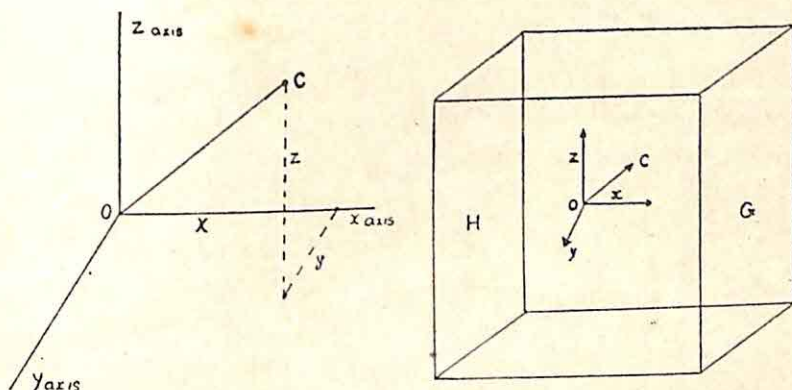


Fig. I.15

The collisions being perfectly elastic, the molecule after striking the wall G with velocity x_1 returns with exactly the same velocity but in opposite direction. The momentum of the molecule just when it strikes is mx_1 and when it rebounds, the momentum is $-mx_1$. The change of momentum due to a collision is therefore, $mx_1 - (-mx_1) = 2mx_1$.

It is obvious that after its collision with the wall G , it will travel a distance l to make an impact on the opposite wall H and then return to G again. So, after moving a distance of l every time, it will make an impact on a wall. The total number of collisions the molecule makes on the two opposite walls in unit time

would be $\frac{x_1}{l}$.

Therefore, the total momentum imparted to the two opposite walls G and H by this molecule per second = $\frac{x_1}{l} \times 2mx_1 = \frac{2mx_1^2}{l}$.

If we now consider the directions along Y -axis and Z -axis, the momentum imparted on the corresponding pairs of walls by the collisions of this molecule

would be $\frac{2my_1^2}{l}$ and $\frac{2mz_1^2}{l}$.

Hence, the net momentum imparted on all the six walls by the collisions of this molecule per second is $\frac{2m(x_1^2 + y_1^2 + z_1^2)}{l} = \frac{2mc_1^2}{l}$.

Next, we consider all the molecules having different velocities $c_1, c_2, c_3, \dots$ etc.

The change of momentum per second from collisions of all the molecules on all the walls would be

$$\begin{aligned} & \frac{2mc_1^2}{l} + \frac{2mc_2^2}{l} + \frac{2mc_3^2}{l} + \dots + \frac{2mc_n^2}{l} \\ &= \frac{2m}{l}(c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2) \\ &= \frac{2mNc^2}{l} \end{aligned}$$

where c^2 is the mean square velocity.

This change of momentum per unit time is the force F exerted by the molecules (Newton's Law) on all the walls.

$$\text{i.e.,} \quad F = \frac{2mNc^2}{l}$$

The pressure of the gas P is the force per unit area. There are six walls each of area l^2 . Hence the total force on all the walls,

$$F = 6l^2 \times P.$$

$$\text{That is,} \quad P = \frac{F}{6l^2} = \frac{2mNc^2}{6l^3} = \frac{1}{3} \frac{mNc^2}{v}, \quad \dots (1.27)$$

since $l^3 = v$, the volume of the cube.

$$\text{Hence} \quad Pv = \frac{1}{3} mNc^2 \quad \dots (1.28)$$

The total mass of the gas is mN , so the density of the gas, $\rho = \frac{mN}{v}$. Hence,

$$\text{we have,} \quad P = \frac{1}{3} \rho c^2 \quad \dots (1.29)$$

The expression for pressure may be derived a little more rigidly, as given in appendix I.2.

1.9. The temperature of a gas. According to the kinetic theory, the temperature of a gas is a measure of the average translational kinetic energy of its molecules. That is, the temperature T is a function of E , the kinetic energy. If two gases are at the same temperature, the average kinetic energies of the molecules of the two gases would be the same. Now, we have seen,

$$\begin{aligned} & Pv = \frac{1}{3} mNc^2 \\ \text{i.e.,} \quad & Pv = \frac{2}{3} N \cdot \frac{1}{2} mc^2 = \frac{2}{3} N\epsilon \end{aligned} \quad \dots (1.30)$$

where ϵ is the mean kinetic energy of a molecule.

If we take a gm-mole of gas, (volume V), the number of molecules would be N_0 , Avogadro number. Then,

$$PV = \frac{2}{3} N_0 \epsilon = \frac{2}{3} E \quad \dots (1.31)$$

where E is the kinetic energy of a gm-mole of gas.

From the gas-laws, for a gm-mole we have, $PV = RT$

$$\text{Hence,} \quad E = \frac{3}{2} PV = \frac{3}{2} RT \quad \dots (1.32)$$

Thus, we obtain a quantitative relation between the kinetic energy and the temperature in the absolute scale. Dividing eqn. (1.32) by N_0 on both sides,

$$\epsilon = \frac{3}{2} \frac{RT}{N_0} = \frac{3}{2} kT$$

where $\frac{R}{N_0} = k$, a universal constant, called *Boltzmann constant*.

The mean kinetic energy of a molecule in a gas is proportional to the absolute temperature of the gas.

We can also write, $\frac{1}{2}mc^2 = \frac{3}{2}kT$

$$\left. \begin{array}{l} \text{or } c^2 = \frac{3kT}{m} \\ \text{also, } c^2 = \frac{3RT}{M} \end{array} \right\} \dots (I.34)$$

That is, the mean square velocity is directly proportional to the absolute temperature. When $T = 0$, $c^2 = 0$. Hence, at the absolute zero of temperature, there would be complete cessation of motion. This deduction from kinetic theory is not however strictly true. The quantum theory reveals that at the absolute zero, a little residual energy, called zero-point energy, is still associated with the molecule.

I.10. Derivation of the gas laws from the kinetic theory. The different gas laws which were empirically obtained can be derived from the theory.

(i) *Boyle's Law.* We know,

$$Pv = \frac{1}{3}mNc^2 = \frac{2}{3}N \times \frac{1}{2}mc^2$$

In a given mass of gas, the number of molecules N remains constant. Again, at a constant temperature, the mean kinetic energy of a molecule, $\frac{1}{2}mc^2$, remains constant. Hence, the right hand side is a constant.

$\therefore Pv = \text{constant}$. This is Boyle's Law.

At a constant pressure, $v = \frac{2}{3} \cdot \frac{N}{P} \cdot \frac{1}{2}mc^2 = \frac{2}{3} \cdot \frac{N}{P} \cdot kT = k'T$, which is

Charles' Law.

(ii) *Avogadro's Law.* When equal volumes of two gases are taken at the same pressure and at the same temperature, we have

$$Pv = \frac{1}{3}m_1N_1c_1^2 = \frac{2}{3}N_1 \times \frac{1}{2}m_1c_1^2$$

$$Pv = \frac{1}{3}m_2N_2c_2^2 = \frac{2}{3}N_2 \times \frac{1}{2}m_2c_2^2$$

where (m_1, N_1, c_1) and (m_2, N_2, c_2) denote the mass, number and velocities of the molecules of two gases respectively. Since the temperature is the same, the mean kinetic energy of the molecules of the two gases are equal, i.e.,

$$\frac{1}{2}m_1c_1^2 = \frac{1}{2}m_2c_2^2. \text{ Hence, } N_1 = N_2$$

i.e., equal volumes of the two gases at the same temperature and pressure contain the same number of molecules. This is Avogadro's Law.

(iii) *Dalton's Law of Partial Pressures.* Suppose we take in a box a mixture containing several gases of densities $\rho_1, \rho_2, \rho_3, \dots$, having mean square velocities of the molecules $c_1^2, c_2^2, c_3^2 \dots$ etc. The molecules of all the gases will make impact on the walls. The total pressure then would be, by equation (I.29),

$$P = \frac{1}{3}\rho_1c_1^2 + \frac{1}{3}\rho_2c_2^2 + \frac{1}{3}\rho_3c_3^2 + \dots$$

If the gases were individually present in the same volume, then the individual pressures would be

$$p_1 = \frac{1}{3}\rho_1c_1^2, \quad p_2 = \frac{1}{3}\rho_2c_2^2, \quad p_3 = \frac{1}{3}\rho_3c_3^2 \dots$$

$$\therefore P = p_1 + p_2 + p_3 + \dots$$

i.e., the total pressure is the sum of the partial pressures of the constituents. This is the Dalton's Law of partial pressures.

(iv) *Graham's Law of Effusion.* We have,

$$P = \frac{1}{3}\rho c^2$$

$$\text{or } c = \sqrt{\frac{3P}{\rho}}$$

where c is the root-mean-square velocity. Now the root-mean-square velocity c is proportional to c_a , the average velocity of the molecules (Sec. I.7).

Hence,

$$c_a = k' \sqrt{\frac{3P}{\rho}}$$

When there is a fine orifice on the wall of the vessel containing the gas, the number of molecules which will effuse out is proportional to the average speed of the molecules c_a at any given temperature. That is, the rate of effusion r_e is proportional to c_a .

Hence,

$$r_e = k'.k'' \sqrt{\frac{3P}{\rho}}$$

So, at a given pressure and temperature, the rate of effusion of a gas is inversely proportional to the square-root of its density. This is Graham's Law.

I.11 The Boltzmann constant. The universally accepted value of the Avogadro number N_0 is 6.03×10^{23} . We shall take up the method of its determination in a subsequent chapter. The value of the gas constant R is 8.32×10^7 ergs per degree per mole.

Hence, the magnitude of the Boltzmann constant,

$$k = \frac{R}{N_0} = \frac{8.32 \times 10^7}{6.03 \times 10^{23}} = 1.38 \times 10^{-16} \text{ ergs per degree.}$$

I.12 Calculation of kinetic energy and velocity of a molecule. A few examples are worked out below to illustrate the calculation of kinetic energy and velocity of molecules.

Example. The density of air at N.T.P. is 0.00129 gms/c.c. Calculate the root-mean-square velocity at N.T.P.

$$P = \frac{1}{3} \rho c^2; \text{ hence, } c = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \times 76 \times 981 \times 13.6}{0.00129}} = 4.86 \times 10^4 \text{ cms/sec.}$$

Example : The normal density of hydrogen is 0.000089 gms/c.c., what is the root-mean-square velocity of oxygen at N.T.P.?

Now, density of oxygen = 16×0.000089

$$\therefore c = \sqrt{\frac{3 \times 76 \times 981 \times 13.6}{16 \times 0.000089}} = 4.6 \times 10^4 \text{ cms/sec.}$$

Example : Calculate the kinetic energy of a molecule of hydrogen at 0°C .

$$\epsilon = \frac{E}{N_0} = \frac{3}{2} \frac{RT}{N_0} = \frac{3}{2} \cdot \frac{8.32 \times 10^7 \times 273}{6.03 \times 10^{23}} \\ = 5.678 \times 10^{-14} \text{ ergs.}$$

Example : Calculate the kinetic energy of one gm of oxygen at 47°C .

One gm oxygen = $\frac{1}{32}$ gm-mole.

$$\text{K. E. of a gm-mole, } E = \frac{3RT}{2}$$

$$\therefore \text{K. E. of 1 gm} = \frac{E}{32} = \frac{3RT}{64} = \frac{3}{64} \times 8.32 \times 10^7 \times 320 = 1.24 \times 10^9 \text{ ergs.}$$

Example : At what temperature will the r.m.s. velocity of oxygen be one and half times of its value at N.T.P.?

We know

$$\frac{1}{2} mc^2 = \frac{3}{2} kT \quad \text{or} \quad c \propto \sqrt{T}$$

Suppose the temperature required is T' when the velocity will be $\frac{3}{2}c$.

$$\text{or } \frac{\frac{3}{2}c}{c} = \sqrt{\frac{T'}{T}} = \sqrt{\frac{T'}{273}}, \text{ whence } T' = \frac{9}{4} \times 273 = 614.25^\circ \text{ Abs.}$$

Example : Calculate the number of molecules per c.c. at 27°C in a high vacuum of 10^{-6} mm of mercury.

Suppose there are q molecules still present per c.c.

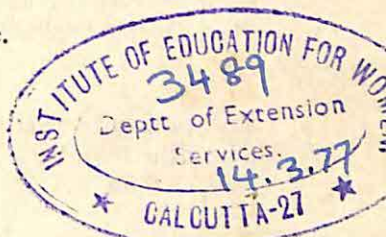
$$q \text{ molecules per c.c.} \equiv \frac{q \times 1000}{N_0} \text{ gm-moles per litre.}$$

Now

$$Pv = nRT$$

$$\text{or} \quad \frac{10^{-6}}{760} \times 1 = \frac{q \times 1000}{N_0} \times .082 \times (273 + 27)$$

$$\text{or} \quad q = \frac{6 \times 10^{23} \times 10^{-6}}{760 \times .082 \times 300 \times 1000} = 3.2 \times 10^{10}$$

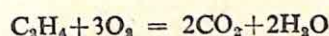


Example : A half-litre bomb at 27°C is filled with C_2H_4 at 1 atm. and oxygen at 5 atm. and the mixture is exploded. Calculate the final pressure if final temperature is (a) 27°C, (b) 127°C. The aq. tension at 27°C is 27 mm.

$$\text{For } C_2H_4 : P_{C_2H_4} \times 0.5 = nRT, \text{ or } n = \frac{1 \times 0.5}{RT} = \frac{0.5}{RT}$$

$$\text{For } O_2 : P_{O_2} \times 0.5 = n'RT, \text{ or } n' = \frac{5 \times 0.5}{RT} = \frac{2.5}{RT}$$

Since



$$\frac{0.5}{RT} \text{ moles of } C_2H_4 \text{ used up } \frac{3 \times 0.5}{RT} \text{ or } \frac{1.5}{RT} \text{ moles of } O_2$$

$$\text{Hence, residual oxygen} = \frac{1.0}{RT} \text{ moles.}$$

$$\text{At } 27^\circ C, \text{ gases present are, } CO_2 \text{ (produced)} = \frac{2 \times 0.5}{RT} = \frac{1.0}{RT} \text{ moles, } O_2 \text{ (left)} = \frac{1.0}{RT}$$

plus water vapour to saturation.

The pressure given by the gases

$$P' \times 0.5 = \left(\frac{1.0 + 1.0}{RT} \right) RT \text{ or } P' = 4 \text{ atmospheres.}$$

The net pressure at 27°C, $P = P' + 27 \text{ mm} = 4.04 \text{ atmospheres.}$

At 127°C, i.e., 400°K, the water produced will all be in gaseous phase and the amount would be equal to that of carbon dioxide,

$$\text{i.e., } O_2 = \frac{1.0}{RT}, \quad CO_2 = \frac{1.0}{RT}, \quad H_2O = \frac{1.0}{RT}$$

∴ Pressure at 400°K would be

$$P \times 0.5 = \frac{3}{R \times 300} \times R \times 400 \text{ or } P = 8 \text{ atmospheres.}$$

I.13 Number of molecules of a gas impinging on unit area of the wall. Suppose N represents the total number of molecules in a container of volume v , the number of molecules per unit volume,

$$n = \frac{N}{v}, \text{ or } dN = ndv \quad \dots (a)$$

This relation will hold true even when we take a very minute volume element dv , which would still contain a large number of molecules.

Again, all directions of molecular velocities are equally probable. Consider each molecule with a vector representing the direction and magnitude of its velocity. Suppose all these vectors start from the origin of a sphere of radius r as in Fig. I.16. The vectors will intersect the surface of the sphere in as many points as there are vectors, i.e., as there are molecules. Since all directions are equally probable, the points of intersections are uniformly distributed on the entire surface. The vectors have to be prolonged, if necessary. The number of such points per unit area of the surface will obviously be $\frac{N}{4\pi r^2}$. Hence in an area ds , the number is given by,

$$dN = \frac{N}{4\pi r^2} ds \quad \dots (b)$$

If, however, the area on the surface of the sphere is expressed in polar co-ordinates, using angles θ and ϕ ,

$$ds = r^2 \sin\theta d\theta d\phi \quad \dots (c)$$

The points in this small area refer to the molecules which have velocities in a direction θ and $\theta+d\theta$, ϕ and $\phi+d\phi$. Let us denote this number of molecules by $d^2N_{\theta\phi}$, then

$$d^2N_{\theta\phi} = \frac{N}{4\pi r^2} r^2 \sin\theta d\theta d\phi = \frac{N}{4\pi} \sin\theta d\theta d\phi \quad \dots (d)$$

Dividing both sides by the total volume, v , we shall get the number of molecules per unit volume having velocities in the directions θ and $\theta+d\theta$, and ϕ and $\phi+d\phi$.

$$d^2n_{\theta\phi} = \frac{n}{4\pi} \sin\theta d\theta d\phi \quad \dots (e)$$

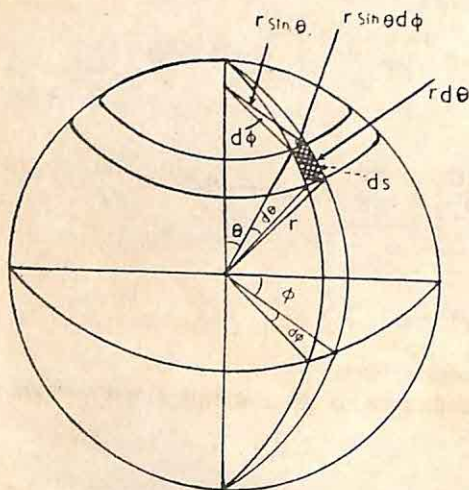


Fig. I.16

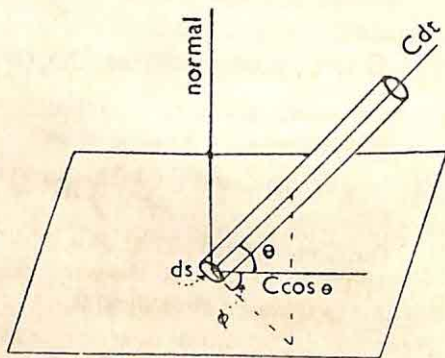


Fig. I.17

We shall then proceed to find out the number of molecules actually striking a small area on a surface in a given time dt . Take a small area ds on the surface which is inclined in directions θ and $\theta+d\theta$, and ϕ and $\phi+d\phi$ to the normal as shown in the figure I.17. These directions we shall specify as $\theta\phi$ -direction. At the first instance let us find out the number of molecules having velocity c moving in $\theta\phi$ -directions which will strike the area ds . On ds as cross-section, draw the cylinder as shown in the figure with a length of $c dt$ units and inclined at $\theta\phi$ -direction. The molecules which are at a distance $c dt$ from the surface would just reach the surface. The molecules of velocity c and direction $\theta\phi$ which are within this cylinder will certainly strike this surface in time dt . Many other molecules also having other velocities and other directions would of course strike the area ds in time dt .

If dn_c denotes the number of molecules per unit volume with velocity c moving in $\theta\phi$ -direction, then from equation (e), we have

$$d^3n_{\theta\phi c} = \frac{dn_c}{4\pi} \sin\theta d\theta d\phi \quad \dots (f)$$

The volume of the cylinder in the figure is

$$dv = ds \times c dt \cos\theta$$

The molecules of velocity c and direction $\theta\phi$ which are present in this volume dv will all strike ds , and this number is

$$\begin{aligned} d^3n_{\theta\phi c} \times dv &= \frac{dn_c}{4\pi} \sin\theta \, d\theta \, d\phi \times ds \cdot c \, dt \cos\theta \\ &= \frac{1}{4\pi} c \, dn_c \cdot \sin\theta \cos\theta \, d\theta \, d\phi \, ds \, dt \end{aligned}$$

Putting $ds = 1$ and $dt = 1$, the number of molecules having velocity c , direction $\theta\phi$ which will strike per unit area per unit time, is

$$\frac{1}{4\pi} c \, dn_c \sin\theta \cos\theta \, d\theta \, d\phi \quad \dots (g)$$

The number of molecules with velocity c coming from all possible directions which will strike per unit area per unit time is obtained by integrating (g) for θ between the limits 0 and $\pi/2$, and integrating for ϕ between the limits zero and 2π . This gives the value

$$Z_c = \frac{1}{4} c \, dn_c \quad \dots (h)$$

Then the total number of collisions per unit area per unit time by molecules with all possible speeds will be given by

$$Z = \int \frac{1}{4} c \, dn_c \quad \dots (i)$$

Now, suppose there are N_1 molecules with velocity c_1 , N_2 molecules with velocity c_2 , etc, then the average velocity c_a is given by

$$c_a = \frac{N_1 c_1 + N_2 c_2 + \dots}{N_1 + N_2 + \dots} = \frac{\sum N_i c_i}{N} = \frac{\sum \frac{N_i c_i}{v}}{\frac{N}{v}} = \frac{\sum n_i c_i}{n}$$

If the molecules have a continuous distribution and n denotes the number of molecules, then

$$c_a = \frac{\sum c \, dn_c}{n} = \frac{1}{n} \int c \, dn_c \quad \dots (j)$$

Substituting (j) in (i); we have the number of molecules striking the unit area in unit time,

$$Z = \frac{1}{4} n c_a \quad \dots (I.35)$$

$\therefore$ mass of gas striking per unit area, $\mu = \frac{1}{4} m n c_a$

$$= \frac{1}{4} m (N_0/v) \cdot c_a = \frac{1}{4} \frac{M \cdot P}{RT} \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{M}{2\pi RT}} \cdot P \quad \dots (I.35a)$$

Pressure in a gas. We have just seen that the number of $\theta\phi c$ -collisions per unit area per unit time is given by

$$\frac{1}{4\pi} c \, dn_c \sin\theta \cos\theta \, d\theta \, d\phi.$$

The direction of impact being θ , the angle of reflection on rebounding will also be θ , assuming perfectly elastic collisions. The velocity c also remains unaltered. The normal component of the velocities would be $c \cos\theta$ before collision and $-c \cos\theta$ after collision. The change in momentum per collision is $mc \cos\theta - (-mc \cos\theta) = 2mc \cos\theta$

The change in momentum per unit time per unit area due to $\theta\phi c$ -collisions only would be,

$$(2mc \cos \theta) \left(\frac{1}{4\pi} c dn_c \sin \theta \cos \theta d\theta d\phi \right) \\ = \frac{1}{2\pi} mc^2 dn_c \sin \theta \cos^2 \theta d\theta d\phi$$

If we consider all the c -velocity molecules from all possible directions, the change of momentum would be,

$$\frac{1}{2\pi} (mc^2 dn_c) \int_0^{\pi/2} \int_0^{2\pi} \sin \theta \cos^2 \theta d\theta d\phi \\ = \frac{1}{2\pi} (mc^2 dn_c) \left(\frac{1}{3} \right) (2\pi) \\ = \frac{1}{3} mc^2 dn_c$$

Next let us take all the molecules having all the possible velocities. The total change of momentum per unit time per unit area, (i.e., the pressure P) would be,

$$P = \frac{1}{3} m \int c^2 dn_c \quad \dots (I.36)$$

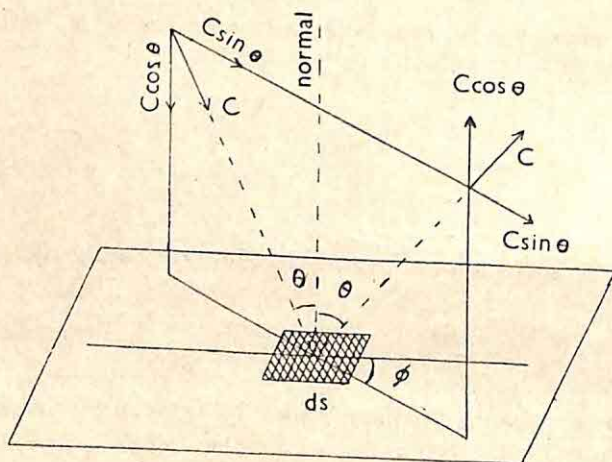


Fig. I.18

We know, $\bar{c^2} = \frac{\sum n_1 c_1^2}{n}$, where $\bar{c^2}$ is the mean-square velocity.

The molecules have a continuous distribution of velocities.

$$\therefore \frac{\sum n_1 c_1^2}{n} = \frac{1}{n} \int c^2 dn_c$$

remembering dn_c is the number of molecules having the velocity c .

$$\text{Hence, from (I.36)} \quad P = \frac{1}{3} m n \bar{c^2}$$

$$\text{Since } n = \frac{N}{v}, \text{ we have } P v = \frac{1}{3} m N \bar{c^2}$$

This is the same relation as derived earlier in equation (I.28)

Effusion. From (I.35) the mass of gas impinging per unit area per unit time is $\frac{1}{4} n m \bar{c}$.

Suppose now, we have a small hole of area ds on the surface. The molecules which would strike this area will effuse out (or escape) through the hole. The weight of the gas effusing out per second, i.e., $\frac{dw}{dt}$, is given by

$$\frac{dw}{dt} = \frac{1}{4} mnc_a \times ds = \frac{1}{4} \rho c_a ds$$

where ρ is the density of the gas. Putting $\frac{w}{\rho} = v'$,

$$\frac{dv'}{dt} = \frac{1}{4} c_a ds$$

That is, the rate of flow of the gas is proportional to the average velocity, as assumed in section I.10(iv).

Anticipating equation (I.41), the average velocity $c_a = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$, we may write the rate of effusion,

$$r_e = \frac{dv'}{dt} = \frac{1}{4} \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} ds$$

or

$$r_e = \frac{\text{constant}}{\sqrt{M}}$$

which is Graham's law.

I.14. Maxwell's Law of Distribution of molecular velocities. We have assumed that the molecules of a gas have different velocities. It is then necessary to know how many molecules may possess a velocity of a given magnitude. Maxwell (1859) successfully tackled this problem for the first time. Based on the rules of probability, he derived a distribution function of the velocities amongst the molecules, which is commonly known as the Maxwell's Law of distribution of velocities. We shall give here, in essence, the distribution function as derived by Maxwell.

The following should however be borne in mind in dealing with this problem : (i) The number of molecules present per unit volume at any point is the same and this number is enormously large even at very low pressures. (ii) Even in a very small element of the volume, these molecules are in chaotic motion and the distribution of velocities would equally apply. As regards the molecular velocities the isotropic behaviour is assumed. (iii) The velocities of individual molecules are continuously changing but at any instant the percentage or fraction of the total number of molecules possessing a given velocity, remains constant. This is sometimes mentioned as the 'steady state' of the gas.

Suppose the number of molecules present per c.c. of the gas is n . Consider a molecule whose velocity is c . Let c_x, c_y, c_z be its components along three rectangular axes (X, Y , and Z -axes). Then

$$c^2 = c_x^2 + c_y^2 + c_z^2 \quad \dots (I)$$

Now the probability of this molecule to have its X -component velocity in the vicinity of c_x , say between c_x and $c_x + dc_x$, will depend upon (a) some function of c_x and (b) the magnitude of dc_x , the permitted range. That is, the probability W_x is given by,

$$W_x = f(c_x)dc_x$$

Maxwell then assumed that for this purpose the three components c_x, c_y and c_z , may be considered independent of one another, such that the probabilities of the molecule to have velocity-components in the ranges c_y and $c_y + dc_y, c_z$ and $c_z + dc_z$ will be the same as the X -component. That is,

$$W_y = f(c_y)dc_y \quad \text{and} \quad W_z = f(c_z)dc_z$$

The nature of the function f in all the three cases, due to isotropicity, should also be identical.

This assumption of the independence of the components is certainly not obvious and is indeed a weak-point of the theory. It can best be justified by the fact that the theory predicts a distribution in agreement with experiment.

The probability that all the three components would lie between c_x and $c_x + dc_x$, c_y and $c_y + dc_y$, c_z and $c_z + dc_z$ can be obtained from a product of the individual probabilities.

$$\therefore W_{xyz} = f(c_x)f(c_y)f(c_z) dc_x dc_y dc_z \quad \dots (II)$$

The number of such molecules per c.c. would be

$$dn_{c_x c_y c_z} = nf(c_x)f(c_y)f(c_z) dc_x dc_y dc_z \quad \dots (III)$$

Consider only the molecules having a total velocity c . Suppose the individual components c_x, c_y, c_z are varied by infinitesimal amounts dc_x, dc_y, dc_z . This means that the directions are altered without affecting the speed c . This may be graphically represented as in Fig. I.19. In this diagram, the components c_x, c_y, c_z represented along OX, OY , and OZ , compute the total velocity c . The point P denotes the velocity point (c_x, c_y, c_z) for the given molecule. All the molecules whose velocity-

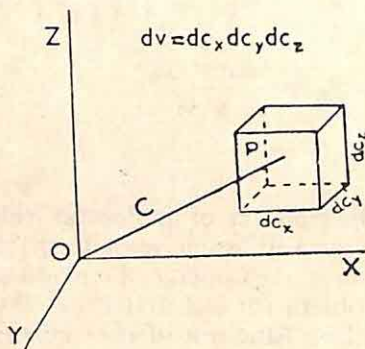


Fig. I.19

component are within the range c_x and $c_x + dc_x$, c_y and $c_y + dc_y$, c_z and $c_z + dc_z$, must have their velocity-points within the volume $dc_x dc_y dc_z$. The number of such molecules would be $nf(c)dc_x dc_y dc_z$, where $\phi(c)$ is some function of c . But we have seen that this number, given by (III), is $nf(c_x)f(c_y)f(c_z) dc_x dc_y dc_z$.

Hence, $f(c_x)f(c_y)f(c_z) = \phi(c) = \psi(c_x^2 + c_y^2 + c_z^2)$

For a given constant value of c , $\psi(c^2)$ is constant, so $\psi(c_x^2 + c_y^2 + c_z^2)$ is constant.

i.e., $f(c_x)f(c_y)f(c_z)$ is constant.

or $df(c_x)f(c_y)f(c_z) = 0$.

... IV

$\therefore f'(c_x)dc_x f(c_y)f(c_z) + f'(c_y)dc_y f(c_x)f(c_z) + f'(c_z)dc_z f(c_x)f(c_y) = 0$

Dividing by $f(c_x)f(c_y)f(c_z)$, we have,

$$\frac{f'(c_x)}{f(c_x)}dc_x + \frac{f'(c_y)}{f(c_y)}dc_y + \frac{f'(c_z)}{f(c_z)}dc_z = 0 \quad \dots (V)$$

Again from (I), since c is constant,

$$c_x dc_x + c_y dc_y + c_z dc_z = 0 \quad \dots (VI)$$

$$\text{i.e., } \beta c_x dc_x + \beta c_y dc_y + \beta c_z dc_z = 0 \quad \dots (VII)$$

where β is an undetermined multiplier.

Combining (V) and (VII).

$$\left(\frac{f'(c_x)}{f(c_x)} + \beta c_x \right) dc_x + \left(\frac{f'(c_y)}{f(c_y)} + \beta c_y \right) dc_y + \left(\frac{f'(c_z)}{f(c_z)} + \beta c_z \right) dc_z = 0$$

The variations dc_x , dc_y and dc_z were arbitrarily chosen for a given velocity c and as such the quantities within each of the parenthesis must be zero.

$$\therefore \frac{f'(c_x)}{f(c_x)} + \beta c_x = 0 ; \text{ i.e., } \frac{f'(c_x)}{f(c_x)} = -\beta c_x$$

On integration, $\log f(c_x) = \frac{-\beta c_x^2}{2} + \log A$

or $f(c_x) = A.e^{-\frac{\beta c_x^2}{2}} = A.e^{-bc_x^2}$
where A and b are constants.

Similarly, $f(c_y) = A.e^{-bc_y^2}$, $f(c_z) = A.e^{-bc_z^2}$

The form of the function f is now known.

Substituting these results in (III),

$$dn_{c_x c_y c_z} = n.A^3.e^{-b(c_x^2 + c_y^2 + c_z^2)} dc_x . dc_y . dc_z \quad \dots (IX)$$

or $dn_{c_x c_y c_z} = nA^3 e^{-bc^2} dc_x . dc_y . dc_z \quad \dots (X)$

To adduce definite values to the number of such molecules, the evaluation of A and b is essential. This may be done in the following way.

Evaluation of 'A' and 'b'. (i) It would be convenient, for this purpose, to change the cartesian co-ordinates to the polar co-ordinates. The volume element $dc_x dc_y dc_z$ would then be equal to $c^2 \sin \theta d\theta d\phi dc$. (vide Fig. I.20). The number of

$$dv = C d\theta \times C \sin \theta d\phi \times dc$$

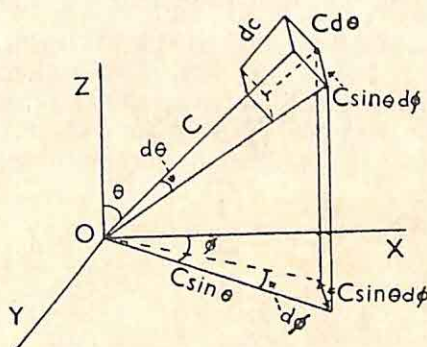


Fig. I.20

molecules having velocities between c and $c+dc$ within the ranges θ and $\theta+d\theta$, ϕ and $\phi+d\phi$ will be

$$dn_{c\theta\phi} = nA^3 e^{-bc^2} c^2 dc . \sin \theta d\theta d\phi \quad \dots (XI)$$

If we integrate this for all possible values of c , θ and ϕ , we shall get the total number of molecules, i.e., n

or $\int dn_{c,\theta,\phi} = nA^3 \int_0^\infty e^{-bc^2} c^2 dc \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi$

or $n = nA^3 \frac{1}{4} \sqrt{\frac{\pi}{b^3}} \times 2 \times 2\pi^*$

whence $A = \sqrt{\frac{b}{\pi}} \quad \dots (XII)$

* For the values of the integrals see appendix I.3.

(ii) From equation (XI), the number of molecules having velocities between c and $c+dc$, irrespective of directions will be given by

$$\begin{aligned} dn_c &= nA^3 e^{-bc^2} c^2 dc \cdot \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi \\ &= 4\pi n \left(\frac{b}{\pi}\right)^{3/2} e^{-bc^2} c^2 dc \quad \dots (XIII) \end{aligned}$$

If we attempt to find out the mean-square velocity of all the molecules, we can represent the same mathematically as

$$\begin{aligned} \overline{c^2} &= \frac{1}{n} \int_{c=0}^{c=\infty} c^2 dn_c \\ &= \frac{1}{n} 4\pi n \left(\frac{b}{\pi}\right)^{3/2} \int_0^\infty e^{-bc^2} c^4 dc \\ &= 4\pi \left(\frac{b}{\pi}\right)^{3/2} \cdot \frac{3}{8} \sqrt{\frac{\pi}{b^5}} \end{aligned}$$

$$\text{or} \quad \overline{c^2} = \frac{3}{2} \cdot \frac{1}{b} \quad \dots (XIV)$$

(which shows that $\frac{1}{\sqrt{b}}$ has the dimensions of velocity.) But from the kinetic theory, we have

$$\overline{c^2} = \frac{3RT}{M} = \frac{3kT}{m} \quad \dots (XV)$$

$$\text{Equating (XIV and XV), } \frac{3kT}{m} = \frac{3}{2b}$$

$$\text{or} \quad b = \frac{m}{2kT} \quad \dots (XVI) \text{ (I.37)}$$

$$\text{and hence} \quad A = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi kT}} \quad \dots (XVII)$$

So, the distribution of molecular velocities may be expressed as :

$$\left. \begin{aligned} dn_c &= 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} c^2 e^{\frac{-mc^2}{2kT}} dc \\ &= 4\pi n \left(\frac{M}{2\pi RT}\right)^{3/2} c^2 e^{\frac{-Mc^2}{2RT}} dc \end{aligned} \right\} \quad \dots \text{ (I.38)}$$

Graphical representation. The distribution function may be written as

$$\frac{dn_c}{dc} = n \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \left(\frac{m}{kT}\right)^{3/2} c^2 e^{\frac{-mc^2}{2kT}}$$

For a given gas, the theoretical curve can be constructed at any given temperature, by evaluating $\frac{dn_c}{dc}$ from the right hand side by putting different values of c ranging between 0 and ∞ . The curve obtained in this way is shown in Fig. I.21.

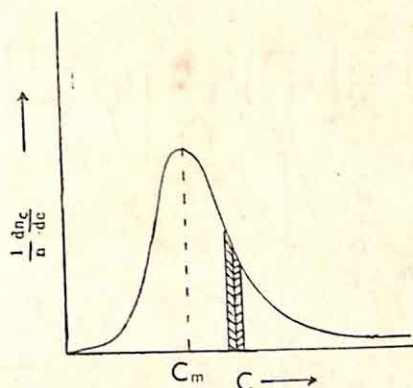


Fig. I.21. The velocity distribution (Maxwell)

An examination of this curve reveals the following :

(i) The number of molecules having very small velocities ($\text{Lt } c \rightarrow 0$) or very high velocities ($\text{Lt } c \rightarrow \infty$) is practically negligible.

(ii) The number of molecules with a certain velocity range c and $c+dc$ is determined from the area given by the product of the ordinate and the velocity range, as the shaded area in the figure.

(iii) The curve indicates a maxima. The velocity corresponding to this maximum represents the speed possessed by the majority number of molecules. This speed is called the 'most probable velocity.' We may represent this by c_m .

(iv) With variation of temperature, there will be separate curve for every temperature. At higher temperature there will be wider distribution of velocities. That is, the number of molecules having high speed is increased. The maxima therefore shifts to the right and is flattened with rise in temperature. The value of c_m also increases (Fig. I.22). The areas under different curves are the same since the area represents the total number of molecules.

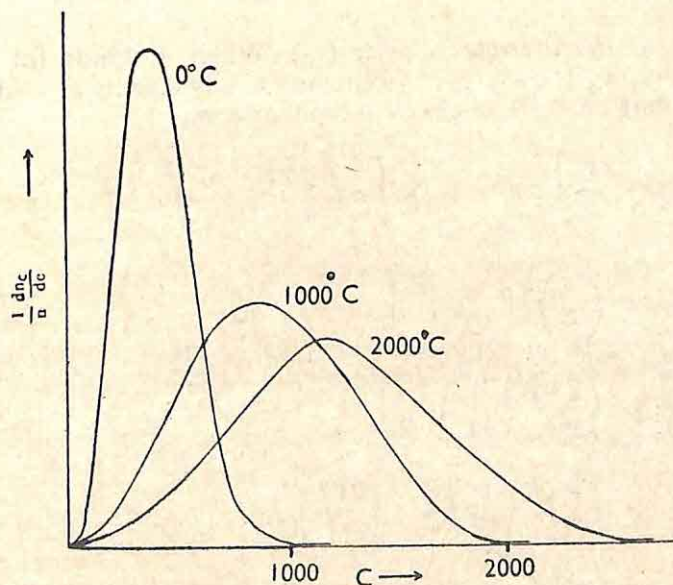


Fig. I. 22. Maxwell's distribution at different temperatures

Calculation of the most probable velocity (c_m). The condition which would satisfy the extremal point in the curve at any given temperature is

$$\frac{d}{dc} (dn_c) = 0.$$

$$\text{i.e.,} \quad \frac{d}{dc} \left[n \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \left(\frac{m}{kT} \right)^{\frac{3}{2}} c^2 e^{\frac{-mc^2}{2kT}} \right] = 0$$

$$\text{or} \quad A_1 \frac{d}{dc} \left[c^2 e^{\frac{-mc^2}{2kT}} \right] = 0$$

where $A_1 = n \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \left(\frac{m}{kT} \right)^{\frac{3}{2}} = \text{constant}$, for a given gas at a fixed temperature.

$$\therefore A_1 c^2 e^{\frac{-mc^2}{2kT}} \left(\frac{-m}{2kT} 2c \right) + A_1 e^{\frac{-mc^2}{2kT}} \cdot 2c = 0$$

$$\text{or} \quad 2c e^{\frac{-mc^2}{2kT}} \left(1 - \frac{mc^2}{2kT} \right) = 0$$

There are three obvious possibilities,

$$(i) \quad c = 0 \quad (ii) \quad e^{\frac{-mc^2}{2kT}} = 0, \text{ when } c = \infty$$

$$\text{or} \quad (iii) \quad \left(1 - \frac{mc^2}{2kT} \right) = 0, \quad \text{when } c = \sqrt{\frac{2kT}{m}}$$

The first two possibilities correspond to the minima : when $c \rightarrow 0$, $dn_c \rightarrow 0$ and when $c \rightarrow \infty$, $dn_c \rightarrow 0$.

The third condition satisfies the maximal point. The velocity corresponding to this is therefore the most probably velocity, i.e.,

$$c_m = \sqrt{\frac{2kT}{m}} \quad \dots (I.40)$$

Calculation of the average velocity (c_a). When c stands for the individual velocity of a molecule, the average molecular velocity c_a may be written as, assuming the velocity may have all values between 0 and ∞ ,

$$\begin{aligned} c_a &= \frac{1}{n} \int_0^\infty c \, dn_c = \frac{1}{n} \int_0^\infty n \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \left(\frac{m}{kT} \right)^{\frac{3}{2}} e^{\frac{-mc^2}{2kT}} c^3 dc \\ &= \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \left(\frac{m}{kT} \right)^{\frac{3}{2}} \int_0^\infty e^{-bc^2} c^3 dc \quad [\text{vide (xvi) above}] \end{aligned}$$

$$= \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \left(\frac{m}{kT} \right)^{\frac{3}{2}} \frac{1}{2b^2} \quad [\text{See app. I.3}]$$

$$= \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \left(\frac{m}{kT} \right)^{\frac{3}{2}} \cdot \frac{1}{2} \left(\frac{2kT}{m} \right)^2$$

$$\text{or} \quad c_a = \sqrt{\frac{8kT}{\pi m}} \quad \dots (I.41)$$

The root-mean-square velocity c may also be derived.

$$\begin{aligned}
 c &= \sqrt{\overline{c^2}} \\
 \text{Hence } \overline{c^2} &= \frac{1}{n} \int_0^\infty c^2 dn_c = \frac{1}{n} \int_0^\infty nc^2 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{\frac{-mc^2}{2kT}} c^2 dc \\
 &= 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_0^\infty c^4 e^{\frac{-mc^2}{2kT}} dc \\
 &= \frac{2}{\sqrt{\pi}} \left(\frac{2kT}{m} \right) \int_0^\infty x^{\frac{3}{2}} e^{-x} dx \quad \left(\text{Putting } x = \frac{mc^2}{2kT} \right) \\
 &= \frac{2}{\sqrt{\pi}} \left(\frac{2kT}{m} \right) \left(\frac{3}{2} \right) \left(\frac{\sqrt{\pi}}{2} \right) \quad (\text{app. I.3}) \\
 &= \frac{3kT}{m}
 \end{aligned}$$

So, we know :

Most probable velocity, $c_m = \sqrt{\frac{2kT}{m}}$

and Average velocity, $c_a = \sqrt{\frac{8kT}{\pi m}}$

Root-mean-square velocity, $\sqrt{\overline{c^2}}$ or say, $c = \sqrt{\frac{3kT}{m}}$

Hence $c_m : c_a : c = 1 : 1.1284 : 1.2284$

This is graphically shown in Fig. I.23.

Hence, $c_a = 0.92c$

$c_m = 0.816c$

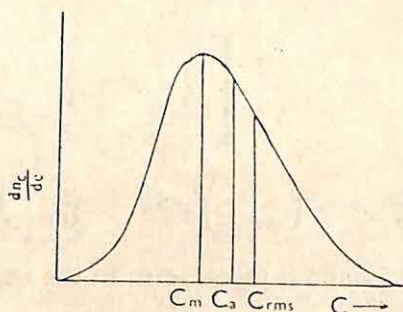


Fig. I.23

I.15 Distribution Law of kinetic energy. Maxwell's relation (eqn. I.38) also enables us to find out how the kinetic energy of translation of the molecules are distributed amongst the molecules. We can determine the number of molecules having kinetic energies in the range ϵ and $\epsilon + d\epsilon$ in the following way:

Since, $\epsilon = \frac{1}{2} mc^2$, or $c = \sqrt{\frac{2\epsilon}{m}}$,

We have, $2c dc = \frac{2}{m} d\epsilon$

Hence
$$c^2 dc = \frac{c}{m} d\epsilon = \frac{1}{m} \sqrt{\frac{2\epsilon}{m}} d\epsilon = \frac{\sqrt{2\epsilon}}{(m)^{\frac{3}{2}}} d\epsilon$$

From Maxwell-relation,

$$dn_c = 4\pi n \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{\frac{-mc^2}{2kT}} c^2 dc$$

$$\therefore dn_\epsilon = 4\pi n \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{\frac{-\epsilon}{kT}} \cdot \frac{\sqrt{2\epsilon}}{m^{\frac{3}{2}}} d\epsilon$$

or
$$dn_\epsilon = \frac{2n \sqrt{\epsilon}}{\sqrt{\pi} (kT)^{\frac{3}{2}}} e^{\frac{-\epsilon}{kT}} d\epsilon \quad \dots (I.42)$$

This gives the required distribution.

It is often necessary to know the fraction of molecules in a gas having kinetic energies exceeding a given value ϵ_1 . Suppose, the number of molecules having energies greater than ϵ_1 is n_{ϵ_1} . Then,

$$n_{\epsilon_1} = \int_{\epsilon_1}^{\infty} dn_\epsilon$$

from eq. (I.42),
$$\frac{n_{\epsilon_1}}{n} = \frac{2}{\sqrt{\pi} (kT)^{\frac{3}{2}}} \int_{\epsilon_1}^{\infty} \epsilon^{\frac{1}{2}} e^{\frac{-\epsilon}{kT}} d\epsilon$$

Suppose $\epsilon = kTx^2$, so that $\epsilon^{\frac{1}{2}} = (kT)^{\frac{1}{2}}x$ and $d\epsilon = kTdx$

Then

$$\begin{aligned} \frac{n_{\epsilon_1}}{n} &= \frac{2}{\sqrt{\pi}} \int_{\sqrt{\epsilon_1/kT}}^{\infty} x \cdot e^{-x^2} d(x^2) \\ &= -\frac{2}{\sqrt{\pi}} \int_{\sqrt{\epsilon_1/kT}}^{\infty} x d(e^{-x^2}) \\ &= -\frac{2}{\sqrt{\pi}} \left[\left\{ x \cdot e^{-x^2} \right\}_{\sqrt{\epsilon_1/kT}}^{\infty} - \int_{\sqrt{\epsilon_1/kT}}^{\infty} e^{-x^2} dx \right] \end{aligned}$$

or
$$\frac{n_{\epsilon_1}}{n} = 2 \left(\frac{\epsilon_1}{\pi kT} \right)^{\frac{1}{2}} e^{\frac{-\epsilon_1}{kT}} + \frac{2}{\sqrt{\pi}} \int_{\sqrt{\epsilon_1/kT}}^{\infty} e^{-x^2} dx$$

When $\epsilon_1 \gg kT$, the second integral term in the right hand side is almost zero. In these circumstances,

$$\frac{n_{\epsilon_1}}{n} = 2 \left(\frac{\epsilon_1}{\pi kT} \right)^{\frac{1}{2}} e^{\frac{-\epsilon_1}{kT}} \quad \dots [I.42 (i)]$$

It may be noted that the quantity on the right side varies rapidly with temperature.

An approximate energy distribution. The energy distribution may be simplified with certain approximations. Restricting the molecular motion to a plane, we may consider only two rectangular components of velocities. Thus we have,

$$\begin{aligned} dn_{x,y} &= nA^2 e^{-b(c_x^2 + c_y^2)} dc_x \cdot dc_y \\ &= nA^2 e^{-bc^2} dc_x \cdot dc_y. \end{aligned}$$

Changing into polar co-ordinates,

$$dn = nA^2 e^{-bc^2} c d\theta dc.$$

Integrating between the limits 0 and 2π for θ , and remembering $b = \frac{M}{2RT}$ and

$A^2 = \frac{b}{\pi}$, we have,

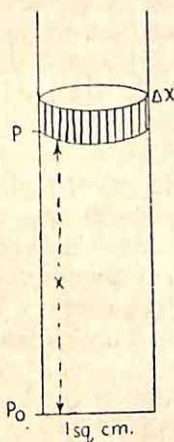
$$dn = n \cdot \frac{M}{RT} e^{-\frac{Mc^2}{2RT}} c dc$$

$$\text{or} \quad \frac{dn}{n} = \frac{1}{RT} e^{-\frac{E}{RT}} dE, \quad (\text{where } E = \frac{1}{2}Mc^2)$$

$$\text{or} \quad \frac{n}{n_0} = e^{-E/RT}$$

$$\text{or} \quad n = n_0 e^{-E/RT} \quad \dots (1.42)$$

where n_0 is the number of molecules in a given state and n is the number of molecules having energy in excess of E per mole more than that possessed in the given state.



The well known barometric formula may be cited to illustrate the general validity of this relation.

The density of the earth's atmosphere diminishes with increasing altitude. Consider a column of the atmosphere with unit cross-section. Imagine a thin slice of gas of thickness dx in this column in which the pressure difference between the upper and lower boundaries of the layer is dP . Then,

$$-dP = \rho g dx$$

where ρ is the density of the gas.

Assuming that the atmosphere behaves like an ideal gas and that the temperature is constant,

$$\rho = \frac{PM}{RT}$$

Hence,

$$-dP = \frac{PMg}{RT} dx$$

or

$$-\frac{dP}{P} = \frac{Mg}{RT} dx$$

Integrating between $P = P_0$ when $x = 0$, and $P = P_1$ when $x = x$,

$$\ln \frac{P_1}{P_0} = -\frac{Mgx}{RT} = -\frac{E_P}{RT}$$

or

$$P_1 = P_0 e^{-\frac{E_P}{RT}} \quad \dots (1.42a)$$

where $E_P = Mgx$ = potential energy at altitude x .

Since the pressures would be proportional to the concentration of molecules at the respective altitudes, we have,

$$n_1 = n_0 e^{-\frac{E_P}{RT}}$$

The Barometric formula is therefore a special case of general relation (1.42).

I.16. Experimental Verification of Maxwell's Law. The validity of the Maxwell distribution Law has been directly tested by a number of investigators. Though the experimental techniques are different, the principle followed was essentially the same in these experiments. We may describe here briefly the outline of one such investigation carried out by Zartman (1931) and, later on, by Ko (1934).

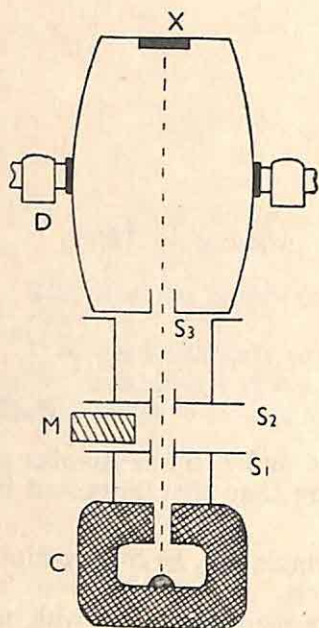


Fig. I.24. Experimental verification of Maxwell distribution Law

A little bismuth was taken in a steel crucible (C), (Fig. I.24) and bismuth was heated by radiation from a hot tungsten filament. The enclosure within the crucible was filled up with bismuth vapour and the temperature was determined by thermocouples. Through a fine channel in the crucible, a narrow molecular beam of bismuth streamed out and passed up through collimating slits, S_1 and S_2 . The slits could be closed by magnetic shutter M , if necessary. Just above the slit S_2 was kept a rapidly revolving drum having a small aperture S_3 on the side which was co-axially adjusted to S_1 and S_2 . Obviously then, during the revolution, once in each turn, when the drum-slit came opposite to the slit S_2 , a small portion of the beam entered the drum. Within the drum, just diametrically opposite to slit was fixed a glass-plate X with a thin coating of Bi. The molecules which entered the slit S_3 ran straight to the opposite wall and deposited on the plate X . Since the molecules have different speeds, all of them would not arrive at the same spot. By the time, the molecules would start from S_3 and reach X , the drum moves through a certain angle. The slower moving molecules would strike at points further and further away. In this way a velocity spectrum was obtained on the glass plate. The whole assembly was kept at high vacuum of nearly 10^{-5} mm and the drum had a revolution of 30000 per minute. The density of the deposit at different points were measured by microphotometry. These densities were proportional to the numbers. The knowledge of the diameter of the drum and the frequency of its revolution enabled the calculation of the velocities of the molecules. The velocity-distribution was found to satisfy the Maxwell relation quite well.

C. REAL GASES : EQUATIONS OF STATE

I.17. Ideal Gases and Real Gases. Careful experiments have revealed that the gas laws such as Boyle's Law, Charles' Law, etc., are only approximately obeyed by the various gases. Even at ordinary pressures, the deviations from the laws are appreciable. It is only at very low pressures and relatively high temperatures, the gases tend to behave in accordance with the gas-laws. Moreover the deviations vary from gas to gas. The equation $PV = RT$ (for one mole) is applicable for approximate calculations only and is quite insufficient for accurate measurement. In order to study the deviations of various gases under different conditions, it was found useful to introduce the concept of an ideal gas. A gas, really a hypothetical one, which follows the gas-laws rigorously under all circumstances, has been named an *ideal gas* or a *perfect gas*, as distinct from the real gases with which we carry out our experiments.

The ideal gas will then observe the relation $PV = RT$ and this may, therefore, be called the equation of state for a perfect gas.

It may be remembered that the gas laws have been derived from the postulates of the kinetic theory. Now that these laws are found to be only approximate, it is obvious that some of the postulates of the theory are inadequate and need modification. The deviations from the ideal laws are primarily due to two factors which are not taken account of in the kinetic theory, namely (i) the volume actually

occupied by the molecules themselves and (ii) the forces of attraction existing between the molecules.

According to the kinetic theory, the volume occupied by the molecules themselves is regarded as negligible compared to the total volume of the gas, *i.e.*, the gas-molecules are regarded as point-masses in an ideal gas. But in a real gas the volume of the molecules themselves is quite appreciable at ordinary pressures. To obtain a clear picture, let us have a quantitative idea.

At N.T.P. one gm-mole occupies 22400 c.c. (approx.) and contains 6×10^{23} molecules. The volume available for each molecule on an average is thus $22400/6 \times 10^{23} = 3.7 \times 10^{-20}$ c.c.

The collision diameter (sec. I.19) of a molecule $\sigma = 2 \times 10^{-8}$ cm. approx., so that the space occupied by each molecule itself is $\frac{4}{3}\pi\sigma^3 = \frac{4}{3}\pi(2 \times 10^{-8})^3 \approx 3.3 \times 10^{-23}$ c.c. That is, at N.T.P.,

the space occupied by the molecule itself is about one-thousandth of the volume it inhabits.

If the pressure be increased to say 10 atmospheres, the volume inhabited by a molecule would be approximately 3.7×10^{-21} while the space occupied by itself will be unaltered. So, the molecule, for its own existence, would take up one percent of the volume, which is by no means negligible.

Again, in the kinetic theory it has been presumed that no inter-molecular force exists and as such the collisions are perfectly elastic, the energy is all kinetic. But, in fact, there does exist a force of attraction between the molecules. On cooling, the gases are converted into liquids when the molecules exhibit appreciable cohesion. This indicates that a similar attraction exists between the molecules in the gas-phase also. A more clear evidence comes from the experiments of Joule and Thomson. When a stream of gas is allowed to pass through a porous plug of cotton or earthen-ware, there is a fall of temperature called Joule-Thomson effect. The only explanation is that the outgoing molecules have to overcome the attraction of molecules from behind and thus have to perform work. The energy thus spent causes the lowering in temperature. In an ideal gas, there is no attractive force between the molecules and hence no cooling would be expected.

Due to inter-molecular attractions, the number of impacts on the wall is restrained, *i.e.*, the number of collisions with the wall would have been greater if there were no attractive force on the colliding molecules from behind. In consequence the pressure exerted on the wall is less. Thus the pressure of one atmosphere actually exerted by oxygen, at 0°C , would be about $(1 + 0.0025)$ atmospheres had it behaved as an ideal one.

It is only at very low pressures when the gas-volume is quite large the space occupied by the molecules themselves becomes negligible comparatively; and because the molecules are then far apart, the force of mutual attraction becomes too feeble. So, at very low pressures, the real gases would satisfy the postulates of the kinetic theory. That is why real gases are observed to obey $PV = RT$ relation at very low pressures. The expression $PV = RT$ is therefore a *limiting law* only.

Before proceeding to obtain a P - V relation which would present the behaviour of real gases in all conditions, we may examine some of the experimental facts to find out the nature of the failure of the ideal gas equation.

I.18. Deviations of the Real Gases from the Ideal Gas-laws. Experiments from different directions have shown that the ideal gas-laws are inadequate for representing the behaviour of the real gases. Some of the results are mentioned here.

(a) In accordance with the Boyle's Law, $PV = \text{constant}$, at a given temperature, the pressure of a gas plotted against its volume would give a rectangular hyperbola. At fairly high temperatures, the P - V isothermals are found to be hyperbolic, though not exactly coinciding with the rectangular ones theoretically predicted. But at temperatures below the critical ones, the P - V curves are far from hyperbolic and really exhibit two discontinuities. The historically famous experiments of Andrews on the study of relations for carbon dioxide are represented in Fig. I.8, which indicates the wide deviations from the Boyle's Law. Similar deviations are observed with other gases too. The failure of the relation, $PV = RT$

to predict a change of state is its major inadequacy. A correct equation of state should account for the behaviour of the substance in both the phases, liquid and gas and also in a state of their co-existence.

(b) The coefficient of expansion (α) of the different gases will be given by (equation I.19),

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = \frac{1}{v} \cdot \frac{nR}{P} = \frac{1}{T}$$

That means that α will be independent of the nature of the gas and will be a function of temperature only. At ordinary pressures, α for different gases is however found to be different and it also depends upon the pressure. This is obviously contrary to the gas-laws. Thus at 500 atmospheres and ordinary temperatures, the coefficients of expansion of hydrogen, nitrogen and carbon dioxide are H_2 , 278×10^{-5} ; N_2 , 315×10^{-5} ; CO_2 , 349×10^{-5} .

(c) Again, from the ideal gas-laws, the coefficient of isothermal compressibility, β should be (equation I.21),

$$\beta = - \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = \frac{1}{v} \cdot \frac{nRT}{P^2} = \frac{1}{P}$$

That is, β should be a function of pressure only and be the same for all gases. Experimentally, however, the coefficient of compressibility is found to be an individualistic property.

In the last century, Ragnault and, later on, Amagat made extensive studies of this aspect. At a given temperature, PV should remain constant according to the gas-laws. Hence, PV plotted against P , should be a straight-line parallel to the P -axis. Amagat made measurements of volume over considerable ranges of pressure. The isothermal curves of various gases obtained are of the nature as shown in Fig. I.25.

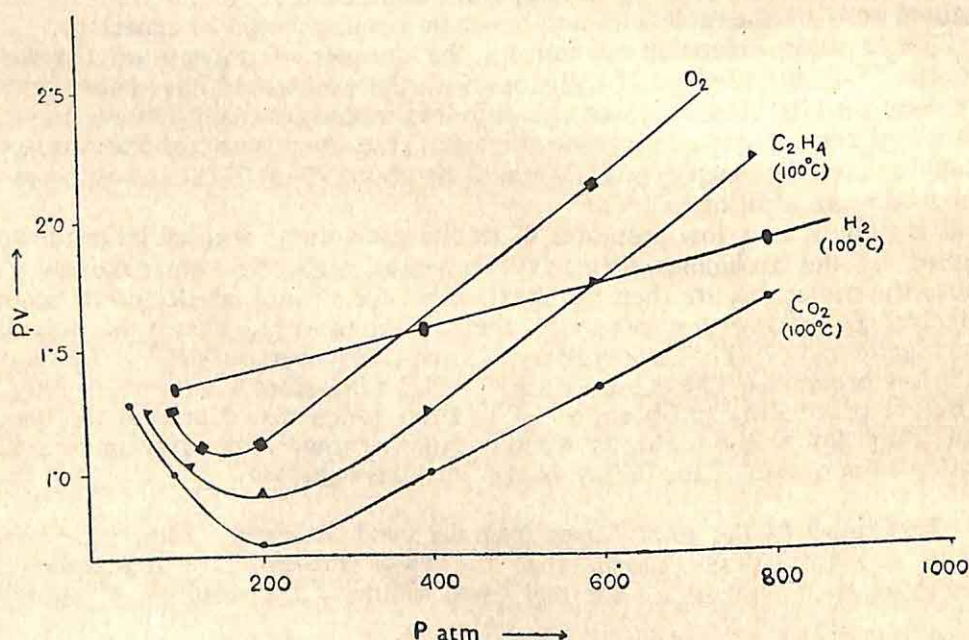


Fig. I.25 PV - P isothermals of gases

None of these curves are linear or parallel to the P -axis. In the cases of carbon dioxide and nitrogen, the PV -value first diminishes, reaches a minimum and then increases, forming a cup, with increase in pressure. In the case of hydrogen, the PV -value begins to increase continuously from zero pressure. Hydrogen, however, is not an exception. It is known that if the temperature be made sufficiently low, hydrogen would also exhibit identical behaviour. It is thus seen that at low

ranges of pressure, the gases are more compressible than what is expected from the ideal laws. In high pressure ranges, the compressibility becomes less than what is ideally expected.

It is also interesting to note the variation of the PV - P relations with temperature. In Fig. I.26 are plotted the PV - P curves of carbon dioxide at different temperatures, which are also typical of other gases. It is seen that the extent of higher compressibility decreases with rise in temperature. As the temperature increases, the troughs of the curves become shallower and flattened. The minimal points of these curves lie approximately on a parabola, shown by the dotted line. At relatively high temperatures, the minimals gradually approach the PV -axis.

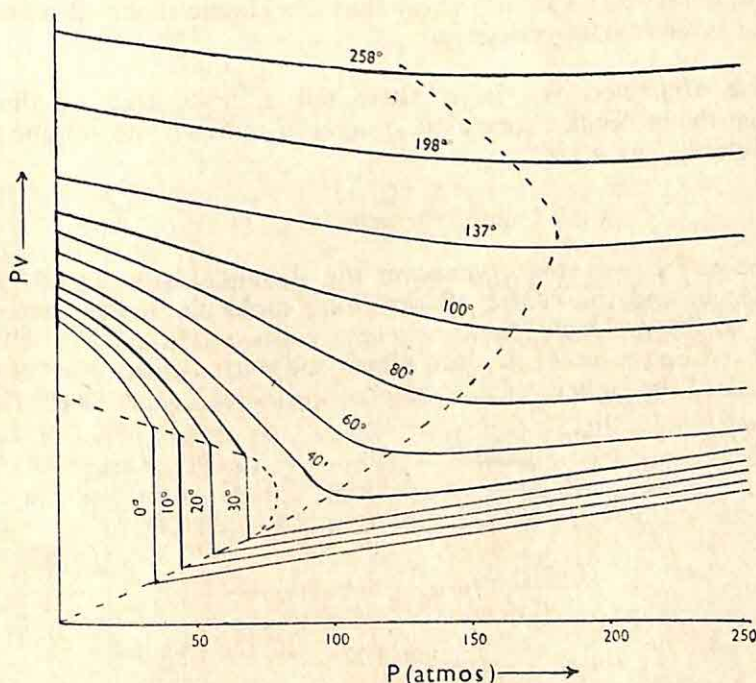


Fig. I.26 PV - P isothermals of carbon dioxide

There exists for every gas a characteristic temperature, where the curve (PV - P) runs sensibly parallel to P -axis from zero pressure to moderate values of pressure (P). It means that at this temperature, the value of PV remains constant for an appreciable range of pressure, i.e., Boyle's Law is obeyed. This temperature is known as the *Boyle temperature* or *Boyle Point* of the gas, T_B . Mathematically we may express the Boyle point as the temperature where

$$\frac{\partial(PV)}{\partial P} = 0, \text{ when } P \rightarrow 0.$$

(d) The cooling due to Joule-Thomson effect is another evidence of the deviation of the real gases from the ideal ones in their behaviour. According to the kinetic theory, the energy of a given quantity of gas depends on the temperature only and is independent of the pressure or volume. But in fact, when a gas is allowed to pass through a fine orifice or porous plug from a high pressure to vacuum (say), the temperature drops down generally. Under certain circumstances, there may also be temperature-rise. This is obviously contrary to the expectations from the theory.

(e) The volume of a gm-mole of any gas at a constant temperature and pressure should be the same according to Avogadro's Law. The gm-molecular volumes of different gases at N.T.P. experimentally measured are found to vary

as shown below. The Avogadro's Law therefore is an approximate one for real gases.

<i>Gas</i>	<i>Molar volume at N.T.P.</i>
Oxygen	22394 c.c.
Nitrogen	22400 c.c.
Hydrogen	22425 c.c.
Carbon dioxide	22264 c.c.
Ammonia	22090 c.c.

All these observations clearly show that the kinetic theory does not correctly represent the behaviour of real gases.

I.19. Collision Diameter. We have attributed a finite size to the molecules. Assuming that the molecules are elastic spheres of radius r , the volume of the body of a molecule only, say b_1 , is

$$b_1 = \frac{4}{3} \pi r^3 \quad \dots (I.43)$$

It can be easily seen, that whenever the distance between the centre of a selected molecule and the centre of any other molecule is less than σ ($= 2r$), the diameter of the molecule, there will be a collision (Fig. I.27). The sphere of radius σ surrounding a molecule, into which the centre of no other molecule can penetrate is called the 'sphere of influence' of the molecule, or the effective volume.

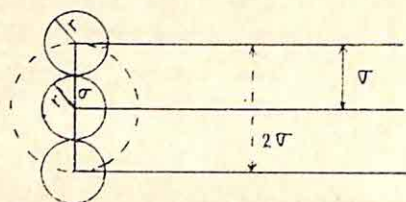


Fig. I.27

The volume of this sphere is β (say). Then

$$\beta = \frac{4}{3} \pi \sigma^3 = \frac{4}{3} \pi (2r)^3$$

i.e.,
$$\beta = \frac{32}{3} \pi r^3$$

Obviously,
$$\beta = 8b_1 \quad \dots (I.45)$$

The radius σ of this sphere of influence really represents the distance of the centres during collision of two molecules and is called the collision-diameter.

I.20. Equations of State for Real Gases. Many attempts have been made during the last hundred years to modify the equation of state for perfect gases and transform it into a form which would represent the P - V - T relations of real gases. All these relations are derived on empirical or semi-empirical basis. Some of these equations are :

Van der Waals : $\left(P + \frac{a}{V^2} \right) (V-b) = RT$

Dieterici : $P(V-b) = RTe^{\frac{-a}{RTV}}$

Berthelot : $\left(P + \frac{a}{TV^2} \right) (V-b) = RT$

$$\begin{aligned}
 \text{Clausius}^1 & : \left(P + \frac{a}{T(V+c)^2} \right) (V-b) = RT \\
 \text{Keyes}^2 & : P = \frac{RT}{V - \beta e^{-a/V}} - \frac{A}{(V+l)^2} \\
 \text{Beattie-Bridgeman}^3 & : P = \frac{RT(1-\epsilon)}{V^2} (V+B) - \frac{A}{V^3} \\
 \text{Saha \& Bose}^4 & : P = -\frac{RT}{2b} \cdot \log \left(1 - \frac{2b}{V} \right) e^{\frac{-a}{RTV}} \\
 \text{Wohl}^5 & : P = \frac{RT}{V-b} - \frac{a}{V(V-b)} + \frac{c}{V^3} \\
 \text{Reinganum}^6 & : \left(P + \frac{a}{V^2} \right) \left(V - be^{-c/RT} \right) = RT \\
 \text{Kammerling Onnes}^7 & : PV = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots \right) \\
 & \text{etc.} \quad \text{etc.}
 \end{aligned}$$

We shall briefly discuss here a few of these equations. One of the earliest and more widely employed equation is that of van der Waals.

I.21. van der Waals' Equation. van der Waals introduced two correction terms one for the pressure and the other for the volume into the ideal gas equation in order to rectify the error for neglecting the inter-molecular attraction and the space occupied by the molecules themselves.

The molecules attract one another with a force which varies inversely as some power of the distance between them and as such the attraction would be appreciable within small distances. A molecule X at the interior of the mass of gas is attracted equally in all directions. These forces would cancel one another and the molecule X would remain unaffected. But a molecule Y very near to the wall would be

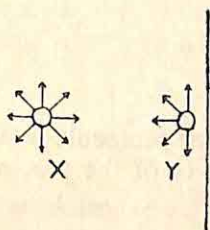


Fig. I.28

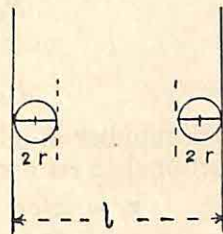


Fig. I.29

pulled inwards by the neighbouring gas molecules and hence has an unbalanced attraction (Fig. I.28). In consequence, the molecule Y will strike the wall with a lesser momentum. This is true for every molecule colliding with the wall. The pressure thus exerted is therefore less than what it would have been in absence of inter-molecular attraction. If this decrease in pressure be denoted by p' , then the ideal pressure would be $P+p'$ where P is the actual observed pressure.

It is also easy to see that the space available for free motion of the molecules is less than the volume the gas occupies. Suppose a molecule A (Fig. I.29), is moving at rt-angles to the two opposite walls of the containing vessel whose distance is l . If the molecules were point masses, the distance to be travelled by a molecule

1. Wiedem 9, 337, 1880.
2. Proc. Nat. Acad. Soc., 3, 323, 1917 ; J Am. Chem. Soc. 41, 589, 1919.
3. J. Am. Chem. Soc. 49, 1665, 1927.
4. Phil. Mag 36, 199, 1918.
5. Z. Phys. chim, 99, 207, 226, 234 (1921).
6. Ann. d. Physik. 10, 334, 1903.
7. Proc. Amst. Acad. 15, 1386, 1913.
Comn. Phys. Lab, Leiden, 188b (1910).

between two successive impacts on the same wall would be $2l$. But the molecules have dimensions, and therefore the distance actually covered by the molecules is $(2l - \sigma)$, where σ is the diameter of the molecule. This is true for all molecules. As a result, the space for free motion of the molecules would be measurably reduced. Suppose v' denotes the reduction in space, then the true volume for motion of the molecules would be $V - v'$ where V is the volume of the gas. We may then write the equation of state, corrected for the volume and the pressure, of a real gas in the form

$$(P + p')(V - v') = RT.$$

van der Waals proceeded to find out the magnitudes of the correction terms p' and v' in the following way.

Pressure correction, p' . During collision a molecule changes its velocity. When it approaches another molecule, there is a drop in velocity. This is followed by an acceleration on separation. Every collision therefore causes a certain loss of time τ . This time τ is a measure of the inter-molecular attraction and is therefore also a measure of p' , the inward pressure.

Let us imagine that the molecule would strike the wall z times per second if there were no inter-molecular attraction. During its journey to make z bombardments on the wall, suppose the molecule makes x inter-molecular collisions. The x collisions will take up $x\tau$ seconds. Now, because of the existence of inter-molecular attraction, the time needed for making z bombardments on the wall would be $1 + x\tau$

seconds. That is, in 1 second it would make $\frac{z}{1+x\tau}$ bombardments. The pressure

is proportional to the rate of bombardments. If P is the observed pressure and P_0 the ideal pressure, (the pressure corrected for inter-molecular attraction), then,

$$\frac{P_0}{P} = 1 + x\tau$$

i.e.,

$$P_0 = P(1 + x\tau) = P + Px\tau$$

Now, x , the number of molecules which the particular molecule would collide with, is proportional to its own velocity c , and the density of the gas, ρ . That is,

$$x = k'c\rho$$

(where $k' = \text{constant}$)

So,

$$Px\tau = Pk'c\rho\tau$$

$$= \frac{1}{3} \frac{mNc^2}{V} \cdot k'c\rho\tau \quad (\text{approximately})$$

$$= \left(\frac{1}{3} (mN)^2 c^3 k' \tau \right) \frac{1}{V^2} \quad \left(\text{since } \rho = \frac{mN}{V} \right)$$

It is assumed that for a definite amount of a given gas, the quantity within the parenthesis remains almost constant, and is substituted by a .

So,

$$Px\tau = \frac{a}{V^2}$$

There is no evident justification for this assumption but nevertheless the value of ' a ' experimentally determined shows sensible constancy unless the temperature is widely varied. This assumption is indeed a weak point in van der Waals' treatment. The pressure of the gas, corrected for molecular attraction then

$$P_0 = P + Px\tau = P + \frac{a}{V^2}$$

The quantity $\frac{a}{V^2}$ is the additional amount of pressure, (p') to be added

to the observed pressure P . This is often called the *cohesive pressure* or *internal pressure*.*

Volume correction, v' . Consider a gm-mol of a gas occupying a volume V . In deducing the ideal gas equation, the molecules were regarded as point-masses and hence the entire volume V was available for movement of each molecule. Since the molecules have definite size, the volume or space available for molecules to move about in real gases would be less. Assuming the molecules to be spherical, suppose r is the radius and $\sigma (= 2r)$ be the diameter of a molecule of the gas, so that the volume of the body of each molecule, $b_1 = \frac{4}{3}\pi r^3$.

When two molecules encounter each other, the distance between the centres of the two molecules would be σ . These cannot approach closer than this. In consequence, as shown in the figure, a space indicated by the dashed circle having a diameter σ , will be unavailable to the pair of colliding molecules. This space, often called 'excluded volume' for the pair of molecules is $\frac{4}{3}\pi\sigma^3$.

Then, the excluded volume for each molecule, $\beta' = \frac{2}{3}\pi\sigma^3$. But the volume of the body of each molecule; $b_1 = \frac{4}{3}\pi r^3 = \frac{1}{8}\pi\sigma^3$.

hence,

$$\beta' = 4b_1.$$

For a gm-mol of the gas, on an average, such excluded volume will be, $4.N_0\beta' = b$ (say), which is a constant.

The volume correction v' is thus b , which is equal to four times the actual volume of the bodies of the molecules. The observed volume should therefore be reduced by this amount (b) in computing the pressure of the gas. The volume V should be replaced by $(V-b)$.

The equation of state, corrected for the two factors, takes the form.

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \quad (\text{for 1 gm-mol}) \quad \dots (I.46)$$

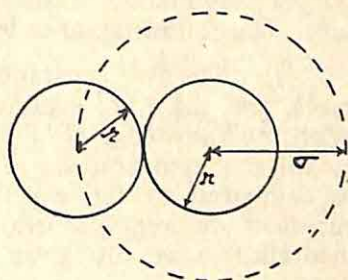
This is known as *van der Waals equation*.

If n gm-mols of gas be present in volume V , the volume of one gm-mol would be V/n . So, we have,

$$\left(P + \frac{a}{(V/n)^2}\right)(V/n-b) = RT.$$

or

$$\left(P + \frac{n^2a}{V^2}\right)(V-nb) = nRT \quad \dots (I.46a)$$



[Excluded volume for a pair of molecules]

* The cohesive pressure $\frac{a}{V^2}$ may also be obtained from the following considerations. The internal pressure will be proportional to the number of molecules colliding with walls. This number is proportional to the density of the gas. Again, the force acting upon each colliding molecule is proportional to the number of molecules in the interior, and this number is also proportional to the density of the gas. Hence, internal pressure is proportional to ρ^2 . Or,

$$p' = k\rho^2 = \frac{a}{V^2} \quad (\text{where } a \text{ is a constant}).$$

I.22. Validity of the van der Waals Equation. Although the two obvious corrections necessary have been introduced in deriving the van der Waals's equation, a critical examination of the equation shows that the equation is not wholly satisfactory. The following considerations would be revealing:

(a) The two constants ' a ' and ' b ' of the equation are different for different gases, and these are experimentally determined, as shown later in section (I.23). With the knowledge of ' a ' and ' b ' for a given gas, its P - V isothermals are plotted at different temperatures (T) from the equation. These isothermals may then be compared to the experimental isothermals (Andrews curves). A set of such curves at different temperatures are shown in Fig. (I.30) for carbon dioxide. The theoretical curves are given in bold lines and the experimental ones in dotted lines.

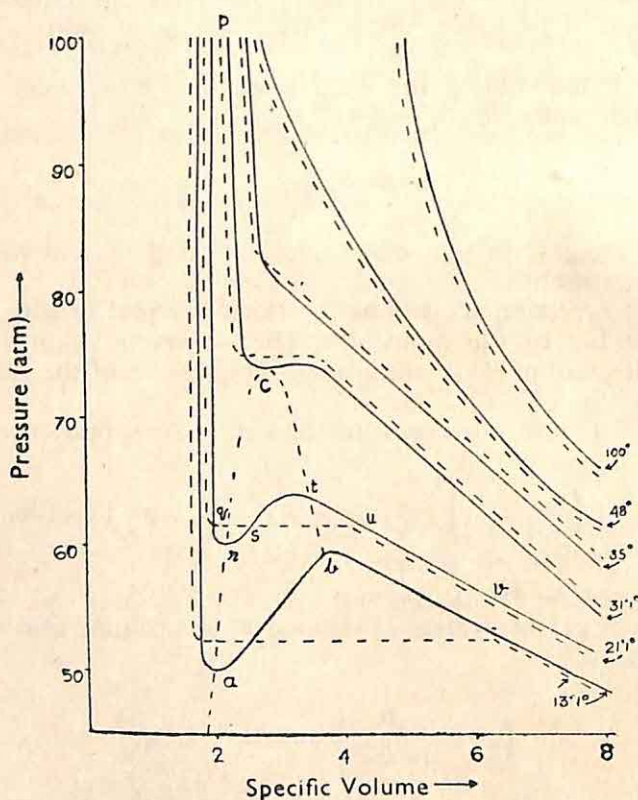


Fig. I.30 P - V isothermals of CO_2

It would be readily seen that at high temperatures the theoretical and the experimental curves coincide and the van der Waals equation is quite satisfactory. But at low temperatures there is a considerable divergence between the experimental and the theoretical curves, specially in the region where we know, the condensation takes place and the liquid and gas are co-existing. At low temperatures, the theoretical curves show a $\sim$ -shaped formation with minima and maxima in the region corresponding to the straight horizontal portion of the experimental

curves. Let us examine one such curve, say at 21.1°C , as represented theoretically by $pqrstuv$. The liquid range pq almost follows the experimental curve, so also the purely gaseous range uv . But the portion $qrstu$ remarkably differs from the experimental straight path qsu , when liquid and gas are present together. The portion ut represents undercooled gas, (this portion being part of the isothermal of a little higher temperature), and can sometimes be experimentally realised. Similarly, the portion qr which represents superheated liquid, may also be obtained under certain conditions. But the portion rst of the theoretical curve (minimum to maximum) represents a condition in which the volume of the system would increase with pressure. This is the most unstable state of the system and can never be realised experimentally. So, in this range, the equation of van der Waals fails to represent the behaviour of the gases.

That van der Waals equation is decidedly an improvement over the ideal equation of state will be borne from the data in Table A below where we may compare the observed pressure of a mole of gas with those calculated from the two equations. In Table B the PV -values observed and calculated from van der Waals are compared.

TABLE A (Temp. 100°C)

Gas	Pressure observed	Pressure calculated from			
		ideal eqn.	deviation	van der Waals	deviation
Hydrogen	75	72.3	- 3.6%	75.7	+ 0.9%
	100	95.0	- 5.0%	100.8	+ 0.8%
Carbon dioxide	75	92.3	+17.3%	73.2	- 2.3%
	100	133.5	+33.5%	95.8	- 4.2%

TABLE B (Ethylene at 293°K)

Pressure (atm.)	PV (arbitrary units)	
	obs.	van der Waals
1	1.0	1.0
32	0.914	0.895
74	0.420	0.384
110	0.454	0.456
233	0.807	0.805
330	1.067	1.067

(b) Further examination of the isothermal of Fig. I.30 shows that when we proceed from the lower to the higher temperatures, the $\sim$ -shaped portions of the curves gradually diminish and the maximum and the minimum points come closer and closer. The $\sim$ -shaped region including the maximum and minimum points correspond to the range of condensation of the gas. The maximum and the minimum points actually coalesce at a point C in the curve corresponding to the critical temperature T_c . Above this temperature, liquefaction is not possible and the maximum-minimum display of the curve is not seen. The point C is therefore the critical point. Since the maximum and the minimum pts. have coalesced at C ,

this point is a point of inflexion, where the first differential $\left(\frac{\partial P}{\partial V}\right)_T$ and the

second differential $\left(\frac{\partial^2 P}{\partial V^2}\right)_T$ should both be equal to zero. That is,

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

At the critical point, $T = T_c$. Then, from above,

$$\frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3} \quad \dots (i)$$

$$\frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4} \quad \dots (ii)$$

$$\text{Dividing (i) by (ii),} \quad \frac{V_c-b}{2} = \frac{V_c}{3}, \quad \text{or } V_c = 3b \quad \dots (iii)$$

$$\text{Substituting (iii) in (i),} \quad T_c = \frac{2a(V_c-b)^2}{RV_c^3}, \quad \text{or } T_c = \frac{8a}{27Rb}$$

$$\text{So, } P_c = \frac{RT_c}{V_c-b} - \frac{a}{V_c^2} = \frac{8a}{27b} \cdot \frac{1}{(3b-b)} - \frac{a}{9b^2}, \quad \text{or } P_c = \frac{a}{27b^2}$$

Thus, for a van der Waals gas, the critical constants are given by,

$$V_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27Rb} \quad \dots (I.47)$$

The equations in (I.47) may be transformed to express the van der Waals constants 'a' and 'b' in terms of critical constants.

$$\left. \begin{aligned} a &= \frac{9}{8} RT_c V_c & b &= \frac{1}{8} \frac{RT_c}{P_c} \\ a &= 3P_c V_c^2 & b &= \frac{1}{3} V_c \\ a &= \frac{27}{64} \frac{R^2 T_c^2}{P_c} \end{aligned} \right\} \quad \dots (I.48)$$

It can also be shown that the ratio $\frac{RT_c}{P_c V_c}$, often called the critical coefficient would be constant.

$$\frac{RT_c}{P_c V_c} = \frac{3a}{27b} \cdot \frac{27b^2}{a} \cdot \frac{1}{3b} = \frac{8}{3} = 2.66 \quad \dots (I.49)$$

van der Waals' equation then predicts that

$$(i) \text{ the ratio } \frac{V_c}{b} \text{ should be equal to 3.00}$$

$$\text{and } (ii) \text{ the critical coefficient } \frac{RT_c}{P_c V_c} \text{ should be equal to 2.66.}$$

The critical constants are determined separately by the methods mentioned in sec. I.3. The value of 'b' is obtained by the study of the P - V isothermals at higher temperatures. The values of V_c/b are given in Table C below, which shows the ratio is not strictly a constant and its magnitude is approximately equal to 2.0. In Table

D, the critical coefficients of several substances are given. Here again, the values are much higher than 2.66 and these are not strictly constant. These go to show that van der Waals equation is not an accurate one.

TABLE C

Gas	<i>A</i>	<i>N</i> ₂	<i>H</i> ₂	<i>CO</i> ₂	<i>O</i> ₂	<i>He</i>
<i>V_c/b</i>	1.41	1.76	2.80	1.86	1.46	2.50

TABLE D

Substance	<i>RT_c/P_cV_c</i>	Substance	<i>RT_c/P_cV_c</i>
Helium	3.084	Methane	3.47
Argon	3.424	Ethane	3.64
Neon	3.086	Benzene	3.75
Hydrogen	3.06	Pentane	3.76
Oxygen	3.42	Octane	3.87
Nitrogen	3.42	Chlorine	3.63
Carbon dioxide	3.49	Chlorobenzene	3.78
Sulphur dioxide	3.61	Carbontetrachloride	3.68
Water	4.39	Ether	3.81
Ethyl alcohol	4.02	Ammonia	4.12

(c) We have seen from the Amagat's curves (*PV*—*P* isothermals) that at the Boyle temperature, a real gas tends to obey Boyle's Law. The minimum of the *PV*—*P* curve is on the *PV*-axis (i.e., *P* = 0).

Hence for the Boyle point, *T_B*, at *P* = 0, $\left[\frac{\partial(PV)}{\partial P} \right]_T = 0$.

The van der Waals equation, $P = \frac{RT}{V-b} - \frac{a}{V^2}$, may be written as

$$PV = \frac{RTV}{V-b} - \frac{a}{V}.$$

Differentiating at constant temperature,

$$\begin{aligned} \left[\frac{\partial(PV)}{\partial P} \right]_T &= \left[\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{a}{V^2} \right] \left(\frac{\partial V}{\partial P} \right)_T \\ &= \left[\frac{-bRT}{(V-b)^2} + \frac{a}{V^2} \right] \left(\frac{\partial V}{\partial P} \right)_T \end{aligned}$$

So, at the Boyle point, where $\left[\frac{\partial(PV)}{\partial P} \right]_T = 0$, we have $\frac{bRT_B}{(V-b)^2} = \frac{a}{V^2}$,

remembering $\left(\frac{\partial V}{\partial P} \right)_T$ cannot be zero.

$$\text{Hence} \quad T_B = \frac{a}{Rb} \left(\frac{V-b}{V} \right)^2.$$

Since when *P* → 0, the volume *V* will be infinitely large, i.e., *V*—*b* ≈ *V*

$$\therefore T_B = \frac{a}{Rb}$$

From van der Waals equation, we have seen (eqn. I.47).

$$T_c = \frac{8a}{27Rb}$$

Hence, the ratio

$$\frac{T_B}{T_c} = \frac{27}{8} = 3.375 \quad \dots (I.50)$$

The experimental determinations, however, show that T_B/T_c is almost constant but the magnitude of the ratio approaches 2.98 instead of 3.375. The van der Waals equation, therefore, is only qualitatively valid.

TABLE

Gas	He	Ne	A	H ₂	O ₂	N ₂
T_B/T_c	3.65	3.00	2.73	3.21	2.56	2.72

(d) *Reduced equation of state.* Since the critical constants are definite quantities for a gas, it is possible to express its, P , V , T , the pressure, volume and temperature in any given state as multiples or sub-multiples of the critical values. Let us say,

$$P = \pi P_c, V = \phi V_c \text{ and } T = \theta T_c$$

where π , ϕ and θ which are numbers called reduced pressure, reduced volume and reduced temperature. These numbers indicate how many times the critical values are greater or smaller than the respective given quantities.

The van der Waals equation may then be changed as,

$$\left(P + \frac{a}{V^2}\right) (V - b) = RT$$

or

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right) (\phi V_c - b) = R \theta T_c$$

Substituting the critical constants by equation (I.47) we have,

$$\left(\frac{\pi a}{27b^2} + \frac{a}{9\phi^2 b^2}\right) (3\phi b - b) = R \theta \frac{a}{27bR}$$

or

$$\left(\pi + \frac{3}{\phi^2}\right) (3\phi - 1) = 8\theta$$

This relation in terms of the reduced parameters of the system is called the van der Waals *reduced equation of state*. The most interesting aspect of this relation is that it would be applicable to all gases, since it is independent of the constants a , b and R .

The equation implies that if two substances have the same reduced pressure π (i.e., their pressures are π times their respective critical pressures) and are also at the same reduced temperature θ , (i.e., their temperatures are θ times their respective critical temperatures), then their reduced volumes ϕ should be the same, (i.e., the ratio $\frac{V}{V_c}$ should be the same). Substances under such conditions are said

to be in corresponding states and the principle laid above is called the *law of corresponding states*.

It gives us a clue to test the validity of the van der Waals equation from which this relation is derived. By maintaining different gases at the same π and θ , we can find out if ϕ is the same. In the table below are incorporated the data for a number of gases, which show that the law of the corresponding states is approximately obeyed. That is, van der Waals equation is not quantitatively valid and

is only an approximate one. The equation can be tested in any homogeneous phase liquid or gas.

CORRESPONDING VOLUMES OF DIFFERENT SUBSTANCES

	$\pi = 0.08846$	$\theta = 0.73-0.75$	
	$\phi_l = \frac{V_{liquid}}{V_c}$	$\phi_g = \frac{V_{gas}}{V_c}$	
Substance	θ_l	ϕ_l	ϕ_g
Benzene	0.7277	0.4065	28.3
Hexane	0.7476	0.4056	29.1
Octane	0.7544	0.4006	29.4
Chlorobenzene	0.7345	0.4028	28.5
Carbon tetrachloride	0.7241	0.4078	27.5
Ether	0.7380	0.4030	28.3
Ethyl acetate	0.7504	0.4001	30.25
Ethyl alcohol	0.7794	0.4061	32.15

I.23. Methods for Determining the Values of 'a' and 'b'. Different methods have been employed to find out the magnitudes of the van der Waals constants 'a' and 'b' for a real gas. The principles of some of these methods are mentioned here.

(i) *From the pressure coefficients.*

We have,
$$P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

$$\therefore \left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b} = \frac{1}{T} \left(P + \frac{a}{V^2} \right)$$

or
$$\frac{a}{V^2} = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

Since pressure coefficient $\beta' = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V$

so
$$\frac{a}{V^2} = TP \left(\beta' - \frac{1}{T} \right) \quad \dots (A)$$

Experimental determination of the pressure-coefficient β' and the parameter of the system, would thus enable us to determine 'a'.

Again since
$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b}$$

$$\therefore b = V - R \left/ \left(\frac{\partial P}{\partial T} \right)_V \right. = V - \frac{R}{\beta' P}$$

The values obtained thus would be applicable in the range β' is determined,

(ii) *From compressibility coefficient, β .*

$$\beta = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{or} \quad \left(\frac{\partial P}{\partial V} \right)_T = - \frac{1}{\beta V}$$

Now
$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \dots (B)$$

and
$$\left(\frac{\partial P}{\partial V} \right)_T = - \frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

i.e.,
$$\frac{1}{\beta V} = \frac{RT}{(V-b)^2} - \frac{2a}{V^3} \quad \dots (C)$$

Solving the equations (B) and (C) with a knowledge of β , the values of a and b can be obtained.

(iii) *From the critical data.* We know, from equation (I.48),

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}, \text{ and } b = \frac{1}{8} \frac{RT_c}{P_c}.$$

The critical constants T_c and P_c are experimentally determined and the values of 'a' and 'b' then calculated. The values obtained are approximate as the van der Waals equation is not accurate in the critical region.

The values of 'a' and 'b' for some common gases are given below (a in atm-litre²/mole², b in litre/mole) :

Gas	H ₂	O ₂	N ₂	CO ₂	NH ₃	CH ₄	A	He
a	0.244	1.36	1.39	3.59	4.17	2.25	1.35	0.034
b	0.027	0.032	0.039	0.043	0.037	0.043	0.032	0.024

The values of both 'a' and 'b' are actually found to vary with temperature and volume at which they are measured. With rise of temperature, the value of a diminishes, i.e., the attractive forces tend to decrease. The value of 'b' also decreases slightly with rise in temperature.

I.24. Modified form of the van der Waals equation. The equation of van der Waals may be written as,

$$P \left(1 + \frac{a}{PV^2} \right) V \left(1 - \frac{b}{V} \right) = RT$$

Or

$$PV = RT \left(1 - \frac{a}{PV^2} \right) \left(1 + \frac{b}{V} \right) \quad (\text{neglecting higher powers})$$

$$= RT \left(1 + \frac{b}{V} - \frac{a}{PV^2} \right)$$

On a first approximation, we may write,

$$PV = RT \left(1 + \frac{Pb}{RT} - \frac{aP}{R^2 T^2} \right) = RT \left[1 + P \left(\frac{b}{RT} - \frac{a}{R^2 T^2} \right) \right]$$

i.e.,

$$PV = RT \left(1 + AP \right)$$

where

$$A = \frac{b}{RT} - \frac{a}{R^2 T^2} = \frac{b}{RT} \left[1 - \frac{a}{bRT} \right]$$

$$= \frac{1}{8} \frac{RT_c}{P_c} \cdot \frac{1}{RT} \left[1 - \frac{27}{64} \frac{R^2 T_c^2}{P_c} \cdot \frac{8P_c}{RT_c} \cdot \frac{1}{RT} \right]$$

$$= \frac{1}{8} \frac{T_c}{P_c} \cdot \frac{1}{T} \left[1 - \frac{27}{8} \frac{T_c}{T} \right]$$

on substitution of 'a' and 'b' by critical constants from eq. I.48.

I.25. The Dieterici Equation.* Another equation of state was proposed by Dieterici in the empirical form,

$$P = \frac{RT}{V-b} \cdot e^{\frac{-a}{RTV}}$$

A theoretical basis for this equation was later developed by Jeans. The volume correction here was evidently the same as that in the van der Waals equation.

For the correction of pressure, Jeans introduced the exponential factor $e^{\frac{-a}{RTV}}$. The reasonings given by Jeans may broadly be stated as follows. A molecule in

* Dieterici, Wiedem, Ann 66, 826, 1898 ; 69, 685, 1899.

coming to the wall from the interior has to overcome the forces of attraction and thereby attains a potential energy higher than that possessed by a molecule in the bulk. In consequence, the density of molecules near the walls will be less than that in the interior. If n and n_0 denote the number of molecules per c.c. at the walls and in the interior, then, according to the distribution law,

$$\frac{n}{n_0} = e^{-\frac{A}{RT}}$$

where A is the excess energy per mole at the walls.

If ρ and ρ_0 , and P and P_0 denote the densities and pressures of the gas at the walls and in the interior, then

$$\frac{n}{n_0} = \frac{\rho}{\rho_0} = \frac{P}{P_0}$$

$$\therefore \frac{P}{P_0} = e^{-\frac{A}{RT}} \quad \text{or} \quad P_0 = P \cdot e^{\frac{A}{RT}}$$

Remembering that P_0 , the pressure in the interior where the cohesive forces from all directions cancel each other, is the ideal pressure, the equation of state is

$$P e^{\frac{A}{RT}} (V-b) = RT$$

or

$$P = \frac{RT}{V-b} \cdot e^{-\frac{A}{RT}}$$

It was, however, soon realised that A depends upon the volume. The equation was then modified to the form,

$$P = \frac{RT}{V-b} \cdot e^{-\frac{a}{RTV}} \quad \dots (I.53)$$

which is known as the *Dieterici Equation*.

On expanding, the equation may be written as,

$$P = \frac{RT}{V-b} \left[1 - \frac{a}{RTV} + \frac{1}{2} \left(\frac{a}{RTV} \right)^2 - \dots \dots \right]$$

$$= \frac{RT}{V-b} - \frac{a}{V(V-b)} \quad (\text{neglecting other terms})$$

At low pressures, the volume is very large so that $V-b \approx V$.

Hence,

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

This is the same as the van der Waals equation. At low pressures therefore, the two equations would respond to the same extent.

The extent of validity of the Dieterici equation may be examined by comparing with experimental results, the V_c/b ratio, the critical coefficient and the Boyle temperature as we did with the van der Waals equation.

(a) V_c/b ratio. Putting $\frac{a}{RT} = c$, we can write the equation as

$$P = \frac{RT}{V-b} e^{-\frac{c}{V}}$$

Hence, $\left(\frac{\partial P}{\partial V} \right)_T = -\frac{RT}{(V-b)^2} \cdot e^{-\frac{c}{V}} + \frac{RT}{V-b} \cdot \frac{c}{V^2} \cdot e^{-\frac{c}{V}}$

$$= -\frac{P}{V-b} + P \cdot \frac{c}{V^2}$$

$$\begin{aligned}\text{And } \left(\frac{\partial^2 P}{\partial V^2} \right)_T &= -\frac{1}{V-b} \cdot \left(\frac{\partial P}{\partial V} \right) + \frac{P}{(V-b)^2} + \frac{c}{V^2} \left(\frac{\partial P}{\partial V} \right) - \frac{2Pc}{V^3} \\ &= \left(\frac{\partial P}{\partial V} \right) \left[\frac{c}{V^2} - \frac{1}{V-b} \right] + P \left[\frac{1}{(V-b)^2} - \frac{2c}{V^3} \right]\end{aligned}$$

At the critical point, both the first and the second differential coefficients would be zero. Hence,

$$\text{when } \left(\frac{\partial P}{\partial V} \right) = 0, \frac{P_c}{V_c-b} = \frac{P_c \cdot c}{V_c^2}, \quad \text{or, } \frac{c}{V_c^2} = \frac{1}{V_c-b} \quad \dots (i)$$

$$\text{and when } \left(\frac{\partial^2 P}{\partial V^2} \right) = 0, \frac{1}{(V_c-b)^2} = \frac{2c}{V_c^3}, \quad \text{or, } \frac{2c}{V_c^3} = \frac{1}{(V_c-b)^2}$$

$$\therefore \frac{V_c}{2} = V_c-b \quad \text{or } V_c = 2b, \text{ i.e., } \frac{V_c}{b} = 2 \quad \dots (ii)$$

$$(b) \text{ Critical coefficient, } \frac{RT_c}{P_c V_c}. \text{ At the critical temperature } T_c, c = \frac{a}{RT_c}$$

$$\text{Now from (i) above, } c = \frac{V_c^2}{V_c-b} = \frac{4b^2}{2b-b} = 4b$$

$$\therefore \frac{a}{RT_c} = 4b, \quad \text{or } T_c = \frac{a}{4bR} \quad \dots (iii)$$

$$\begin{aligned}\text{The critical pressure, } P_c &= \frac{RT_c}{V_c-b} \cdot e^{\frac{-a}{RT_c V_c}} = \frac{a}{4b} \cdot \frac{1}{2b-b} e^{\frac{-4b}{2b}} \\ &= \frac{a}{4b^2} e^{-2} \quad \dots (iv)\end{aligned}$$

$$\text{So, the critical coefficient, } \frac{RT_c}{P_c V_c} = \frac{a}{4b} \cdot \frac{1}{2b} \cdot \frac{4b^2}{a} e^2 = \frac{1}{2} e^2 = 3.695$$

(c) Boyle Temperature, T_B . Multiplying by V , the Dieterici equation is

$$PV = \frac{RTV}{V-b} \cdot e^{-\frac{a}{RTV}}$$

$$\text{Then } \frac{\partial(PV)}{\partial P} = \left\{ \left(\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} \right) e^{-\frac{a}{RTV}} + \frac{RTV}{(V-b)} \cdot \frac{a}{RTV^2} e^{-\frac{a}{RTV}} \right\} \left(\frac{\partial V}{\partial P} \right)$$

We know, $\frac{\partial V}{\partial P} \neq 0$, and at the minimum of Amagat's curves, $\frac{\partial(PV)}{\partial P} = 0$.

$$\therefore \frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{RTV}{V-b} \cdot \frac{a}{RTV^2} = 0$$

$$\text{or } \frac{RTV}{V-b} \left[\frac{1}{V} - \frac{1}{V-b} + \frac{a}{RTV^2} \right] = 0$$

$$\text{or } \frac{a}{RTV^2} = \frac{1}{V-b} - \frac{1}{V} = \frac{b}{V(V-b)}$$

$$\text{or } RT = \frac{a(V-b)}{bV}$$

At the Boyle point, T_B , the minimum lies on the PV -axis ; i.e., $P \rightarrow 0$, $\frac{\partial(PV)}{\partial P} = 0$, and V is very large so that $V-b \approx V$.

$$\therefore RT_B = \frac{a}{b} \cdot \frac{V-b}{V} \approx \frac{a}{b}$$

But from (iii), $RT_c = \frac{a}{4b}$

Hence, $\frac{T_B}{T_c} = 4.0$

We may now make a comparison of these deduced values with those experimentally observed and those obtained from van der Waals.

	van der Waals	Dieterici's	Experimental (average)
V_c/b	3.0	2.0	2.0
$\frac{RT_c}{P_c V_c}$	2.66	3.695	3.6
T_B/T_c	3.375	4.0	2.98

Obviously, the equation of Dieterici is not wholly satisfactory and its limitations are nearly the same as that of van der Waals.

(d) *Reduced equation of state (Dieterici)*. A reduced equation from the Dieterici's equation may also be easily derived. As before we put,

$$\pi = \frac{P}{P_c}, \quad \phi = \frac{V}{V_c}, \quad \theta = \frac{T}{T_c}$$

Then

$$P = \frac{RT}{V-b} \cdot e^{-\frac{a}{RTV}}$$

or

$$\pi P_c = \frac{R\theta T_c}{\phi V_c - b} e^{\frac{-a}{R\theta T_c \phi V_c}}$$

Substituting the critical values from (ii, iii, and iv), $\pi e^{-2} = \frac{\theta}{2\phi-1} \cdot e^{\frac{-2}{\theta\phi}}$

or

$$\pi(2\phi-1) = \theta \cdot e^{2-\frac{2}{\theta\phi}} \quad \dots (1.54)$$

This is the desired reduced equation of state.

I.26. The Berthelot Equation.* The next equation we shall consider is the one empirically proposed by Berthelot, in the form :

$$\left(P + \frac{a}{TV^2}\right) \cdot (V-b) = RT \quad \dots (1.55)$$

The form of the equation is the same as that of the van der Waals except that the cohesive pressure correction is $\frac{a}{TV^2}$ instead of $\frac{a}{V^2}$.

Berthelot, however, proceeded to modify this equation in the light of some experimental results. He started with the assumption that the volume-correction, b , which is the unavailable space for the molecular motion, should be equal to the volume occupied by the liquid subcooled to absolute zero of temperature, say V_{l0} .

* Berthelot, J. physique, 8, 263, 1899.

That is, $b = V_{l0}$. To determine this the Cailletet and Mathias curves were extrapolated to absolute zero. The density of the saturated vapour is then zero. The density of the liquid will be then twice the mean density (obtained from the curve). From the density of the liquid at 0° Abs., the value of V_{l0} was calculated. The determination of critical volume V_c and supercooled liquid volume V_{l0} , showed that the ratio V_c/V_{l0} is approximately 4.0. Berthelot thus assumed that

$$b = \frac{1}{4} V_c \quad \dots (i)$$

For the other two constants a and R of the equation, he accepted the experimental values which were

$$a = \frac{16}{3} P_c V_c^2 T_c \quad \text{and} \quad R = \frac{32 P_c V_c}{9 T_c} \quad \dots (ii)$$

$$\text{Since} \quad b = \frac{1}{4} V_c, \text{ we have } T_c^2 = \frac{a}{6bR} \quad \dots (iii)$$

The original equation may then be transformed.

$$\left(P + \frac{a}{TV^2} \right) (V - b) = RT$$

$$\begin{aligned} \text{or} \quad PV &= RT + Pb - \frac{a}{TV} + \frac{ab}{TV^2} \approx RT + Pb - \frac{aP}{RT^2} \\ &= RT \left[1 + \frac{Pb}{RT} - \frac{aP}{R^2 T^3} \right] \\ &= RT \left[1 + \frac{P}{T} \left(\frac{b}{R} - \frac{a}{R^2 T^2} \right) \right] \end{aligned}$$

Substituting a , b and R by the critical constant values given in (i) and (ii).

$$\begin{aligned} PV &= RT \left[1 + \frac{P}{T} \left(\frac{V_c}{4} \cdot \frac{9T_c}{32P_c V_c} - \frac{16}{3} P_c T_c V_c^2 \cdot \frac{81T_c^2}{(32P_c V_c)^2} \cdot \frac{1}{T^2} \right) \right] \\ &= RT \left[1 + \frac{9}{128} \frac{PT_c}{TP_c} \left(1 - \frac{6T_c^2}{T^2} \right) \right] \quad \dots (I.56) \end{aligned}$$

The equation in this form has been found to be useful in several cases, specially in determination of densities, heat capacities and in the evaluation of free energy changes etc.

Differentiating the equation (I.56) with respect to P , we have

$$\frac{\partial(PV)}{\partial P} = RT \cdot \frac{9}{128} \cdot \frac{T_c}{TP_c} \left(1 - \frac{6T_c^2}{T^2} \right)$$

At the Boyle point, $\frac{\partial(PV)}{\partial P} = 0$, hence,

$$\frac{T_c^2}{T_B^2} = \frac{1}{6} \quad \text{or} \quad \frac{T_B}{T_c} = \sqrt{6} = 2.45 \quad \dots (I.57)$$

which is somewhat lower than the experimental value.

Note : If equation (I.55) be considered, the critical constants would be

$$V_c = 3b, \quad RT_c^2 = \frac{8a}{27b}, \quad \frac{P_c}{RT_c} = \frac{1}{8b}, \quad \text{so} \quad \frac{RT_c}{P_c V_c} = 8/3,$$

the same as in van der Waals.

I.27. The Equation of Kammerling-Onnes. A general and more satisfactory expression for the equation of state is due to Onnes, written as

$$PV = A + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^4} + \frac{E}{V^6} + \dots \quad \dots (I.58)$$

where A, B, C, D , etc. are called first, second, third, etc., *virial coefficients*. These coefficients are constant at a given temperature. The equation is also sometimes expressed in the form :

$$PV = RT \left(1 + \frac{B'}{V} + \frac{C'}{V^2} + \frac{D'}{V^3} + \dots \right) \quad \dots (I.59)$$

On the other hand, Holborn and others use a virial equation in which the product PV is expressed in a power series of the pressure, as

$$PV = A_1 + B_1P + C_1P^2 + D_1P^3 + \dots \quad \dots (I.60)$$

Evidently, $A = A_1 = RT$. It may be mentioned that the second virial coefficient is of major importance in these equations. Other virial coefficients of higher powers of $\left(\frac{1}{V}\right)$ become significant only at high pressures.

The different equations of state mentioned earlier can also be given the virial form. For example, the van der Waals equation may be written as

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{RT}{V} \left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{V^2}$$

$$\text{or } PV = RT \left[1 + \left(b - \frac{a}{RT} \right) \frac{1}{V} + \frac{1}{2} \left(\frac{b}{V} \right)^2 + \dots \right]$$

$$\approx RT \left[1 + \left(b - \frac{a}{RT} \right) \frac{1}{V} \right]$$

Comparing with equation (I.58), the second virial coefficient

$$B = bRT - a \quad \dots (I.61)$$

At the Boyle temperature, the second term must vanish, i.e., $B = 0$

$$\therefore bRT_B - a = 0, \text{ or } T_B = \frac{a}{bR}$$

a result deduced earlier. Again, the Berthelot equation,

$$PV = RT + \frac{9}{128} \cdot \frac{RT_c}{P_c} \cdot \left(1 - \frac{6T_c^2}{T^2} \right) P$$

$$\text{Hence, the virial coefficient, } B = \frac{9}{128} \cdot \frac{RT_c}{P_c} \cdot \left(1 - \frac{6T_c^2}{T^2} \right). \quad \dots (I.62)$$

I.28. Virial Theorem and Equation of State. A rigorous deduction of the equation of state is possible from a consideration of the virial theorem of Clausius. An outline of the theory is first given.

Applying the laws of mechanics to the individual molecules (each of mass m and root mean square velocity c), let us denote the positional co-ordinates of a given molecule by x, y and z . Let X, Y and Z denote the three components of the net external forces acting on the molecule. Then, we have,

$$X = m \frac{d^2x}{dt^2}, \quad Y = m \frac{d^2y}{dt^2}, \quad Z = m \frac{d^2z}{dt^2}. \quad \dots (i)$$

Multiplying these by x, y and z respectively,

$$Xx = mx \frac{d^2x}{dt^2}, \quad Yy = my \frac{d^2y}{dt^2}, \quad Zz = mz \frac{d^2z}{dt^2}. \quad \dots (ii)$$

$$\text{Now } \frac{d}{dt} \left(x \frac{dx}{dt} \right) = x \frac{d^2x}{dt^2} + \left(\frac{dx}{dt} \right)^2$$

$$\text{or } x \frac{d^2x}{dt^2} = \frac{d}{dt} \left(x \frac{dx}{dt} \right) - \left(\frac{dx}{dt} \right)^2 = \frac{1}{2} \frac{d}{dt} \left(\frac{dx^2}{dt} \right) - \left(\frac{dx}{dt} \right)^2 \quad \dots (iii)$$

Similar expressions may also be obtained $y \frac{d^2y}{dt^2}$ and $z \frac{d^2z}{dt^2}$.

Substituting these in (ii) and adding,

$$Xx + Yy + Zz = \frac{m}{2} \frac{d}{dt} \left[\frac{d}{dt} (x^2 + y^2 + z^2) \right] - m \left[\left(\frac{\partial x}{\partial t} \right)^2 + \left(\frac{\partial y}{\partial t} \right)^2 + \left(\frac{\partial z}{\partial t} \right)^2 \right]$$

Since, $c^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2,$

$$Xx + Yy + Zz = \frac{m}{2} \frac{d}{dt} \left[\frac{d}{dt} (x^2 + y^2 + z^2) \right] - mc^2 \quad \dots (iv)$$

This is a relation between the components of the external forces acting on a given molecule with its position and velocity. If we now consider all the molecules, the magnitudes of x^2, y^2, z^2 would be different for each individual but the sum of $(x^2 + y^2 + z^2)$ for all the molecules in the system in equilibrium measured for appreciable time would be constant. That is, the sum $(x^2 + y^2 + z^2)$ would be independent of the time, t . If this were not true, the distances of the molecules from the reference axes would change with time and the gas would change continuously in volume. We can therefore say that the first term on the right hand side of equation (iv) would vanish. Taking all the molecules, we have then

$$\Sigma(Xx + Yy + Zz) = -\Sigma mc^2$$

or

$$-\frac{1}{2}\Sigma(Xx + Yy + Zz) = \frac{1}{2}\Sigma mc^2 = \frac{1}{2}Nmc^2 \quad \dots (v)$$

where N is the total number of molecules.

The term on the left-hand side of this equation was named by Clausius as *virial* of the system. The term on the right-hand side denotes the total kinetic energy of translation of the molecules of the gas. Hence, the total kinetic energy of the gas is its virial. This is the virial theorem of Clausius.

(a) *Ideal Gases*. It is quite simple to derive the equation of state of an ideal gas from the virial theorem. In an ideal gas, there is no intermolecular force. The only force molecules are subject to is the force of impact with the walls of the containing vessel. Suppose the ideal gas is enclosed in a rectangular box with sides of length a, b, c and also suppose the sides are parallel to the co-ordinate axes (Fig. 1.31). The volume of the gas, $V = abc$.

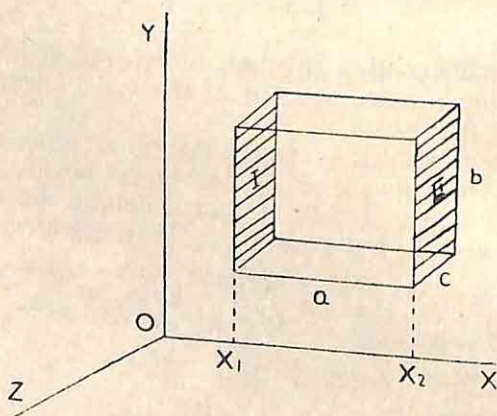


Fig. 1.31

Now consider the two walls I and II of the box which are parallel to the yz plane. The box is so placed that the x -coordinates of the two walls are x_1 and x_2 , such that $x_2 - x_1 = a$. Let P be the pressure. Then the total pressure exerted by the molecules on wall I is $-P.bc$, the $+ve$ direction being along OX .

Therefore, this wall (I) exerts a force $+P.bc$ on the molecules, which is the value of ΣX at x_1 . Hence $\Sigma Xx = +P.bc.x_1$.

For wall II, ΣX is $-P.bc$, therefore $\Sigma Xx = -Pbc.x_2$.

The first component of the virial is thus

$$-\frac{1}{2}\Sigma Xx = -\frac{1}{2}[P.bc.x_1 - P.bc.x_2] = -\frac{1}{2}P.bc.(-a) = \frac{1}{2}PV$$

Similarly, $-\frac{1}{2}\Sigma Yy = \frac{1}{2}PV$ and $-\frac{1}{2}\Sigma Zz = \frac{1}{2}PV$.

Therefore, the virial $-\frac{1}{2}\Sigma(Xx+Yy+Zz) = \frac{3}{2}PV$.

From equation (v), $\frac{3}{2}PV = \frac{1}{2}Nmc^2$ or $PV = \frac{1}{3}Nmc^2$. . . (vi)

This is the ideal gas equation as deduced earlier.

(b) *Real Gases.* In real gases, in addition to the forces of impact on the molecule due to wall-collisions, there are intermolecular forces present. So the virial theorem may be written as,

$$\frac{1}{2}Nmc^2 = -\frac{1}{2}\Sigma(Xx+Yy+Zz)_{wall} - \frac{1}{2}\Sigma(Xx+Yy+Zz)_{int.}$$

The last term on the right-hand determines the virial for the intermolecular forces. The first term on the right hand side, for the virial due to forces of wall-collision, we have seen to be equal to $\frac{3}{2}PV$. Hence,

$$\frac{1}{2}Nmc^2 = \frac{3}{2}PV - \frac{1}{2}\Sigma(Xx+Yy+Zz)_{int.}$$

Since the average kinetic energy of a gas molecule $\frac{1}{2}mc^2 = \frac{3}{2}kT$, we have,

$$3NkT = 3PV - \Sigma(Xx+Yy+Zz)_{int.}$$

$$\text{or } PV = NkT + \frac{1}{3}\Sigma(Xx+Yy+Zz)_{int.} \quad \dots (vii)$$

Now if ϕ denotes the interaction energy between a given pair of molecules at a distance r joining their centres, then

$$F = -\frac{d\phi}{dr} \quad \dots (viii)$$

where F is the force exerted between the molecules. Let the molecules be labelled I and II, as in Fig. I.32.

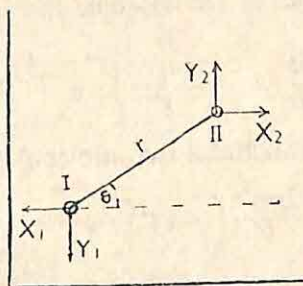


Fig. I.32

The component of F acting on II in the direction of x is $F \cos \theta$,

$$\text{i.e., } \frac{F}{r} (x_2 - x_1)$$

The component of F acting on I in the direction of x is

$$-\frac{F}{r} (x_2 - x_1) \quad \text{i.e., } \frac{F}{r} (x_1 - x_2)$$

Hence, for this pair of molecules, along x -axis,

$$\begin{aligned} \Sigma Xx &= X_1x_1 + X_2x_2 = \frac{F}{r} (x_1 - x_2) x_1 + \frac{F}{r} (x_2 - x_1) x_2 \\ &= \frac{F}{r} (x_2 - x_1)^2 \end{aligned}$$

Similarly $\sum Yy = \frac{F}{r} (y_2 - y_1)^2$ and $\sum Zz = \frac{F}{r} (z_2 - z_1)^2$

Hence for one pair of molecules,

$$\begin{aligned} \sum (Xx + Yy + Zz)_{int} &= \frac{F}{r} \left[(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2 \right] \\ &= \frac{F}{r} \times r^2 = Fr = -r \frac{d\phi}{dr} \end{aligned}$$

Substituting in (vii), we have for all the molecular pairs

$$PV = NkT - \frac{1}{3} \sum r \frac{d\phi}{dr} \quad \dots (ix)$$

We can proceed to find out the summation of the last term in the following way. If n is the number of molecules per c.c. in the bulk (i.e., $n = \frac{N}{V}$) then according to Boltzmann, the number of molecules n_r at a distance r from a given molecule is, $n_r = ne^{-\phi/kT}$ where k is the Boltzmann constant. Assuming radial distribution, the number of molecules present in a shell of thickness dr at a distance r from the given molecule is $n_r \cdot 4\pi r^2 dr$. There will be interaction between the given molecule and each of these molecules, and for every pair, the interaction is $-r \frac{d\phi}{dr}$.

Hence, the total interaction of all molecules of the system with the given molecule is

$$\begin{aligned} \int_0^\infty n_r \cdot 4\pi r^2 dr \cdot \left(-r \frac{d\phi}{dr} \right) &= - \int_0^\infty ne^{-\phi/kT} 4\pi r^3 d\phi \\ &= - \frac{4\pi N}{V} \int_0^\infty e^{-\phi/kT} r^3 d\phi \end{aligned}$$

Consider all the N molecules of the system, the interaction would be, $\sum r \frac{d\phi}{dr}$.

That is,
$$- \sum r \frac{d\phi}{dr} = - \frac{2\pi N^2}{V} \int_0^\infty e^{-\phi/kT} r^3 d\phi,$$

remembering that every pair includes two molecules.

$$\begin{aligned} \text{So, } - \sum r \frac{d\phi}{dr} &= - \frac{2\pi N^2}{V} \left(-kT \left[r^3 e^{-\phi/kT} \right]_0^\infty + 3kT \int_0^\infty e^{-\phi/kT} r^2 dr \right) \\ &= \frac{2\pi N^2 kT}{V} \left(\left[r^3 \right]_0^\infty - 3 \int_0^\infty e^{-\phi/kT} r^2 dr \right) \left[\text{since } \lim_{r \rightarrow \infty} \phi = 0 \right] \\ &= \frac{2\pi N^2 kT}{V} \left(3 \int_0^\infty r^2 dr - 3 \int_0^\infty e^{-\phi/kT} r^2 dr \right) \\ &= \frac{6\pi N^2 kT}{V} \int_0^\infty (1 - e^{-\phi/kT}) r^2 dr \end{aligned}$$

Substituting in (ix), for real gases,

$$PV = NkT + \frac{2\pi N^2 kT}{V} \int_0^\infty (1 - e^{-\phi/kT}) r^2 dr \quad \dots (x)$$

If there be 1 gm-mole of the gas, $N = N_0$ and $N_0 k = R$; hence

$$PV = RT + \frac{2\pi N_0^2 kT}{V} \int_0^\infty (1 - e^{-\phi/kT}) r^2 dr \quad \dots (xi)$$

The form given in (xi) is the rigorous expression for an equation of state for real gases.

van der Waals made the generalisations that

- (i) the molecules are rigid spheres of diameter σ ,
- (ii) the attractive force between the molecules is very feeble and decreases with increase in distance.
- (iii) at close proximity, the molecules experience an intense repulsive force. This repulsive force begins from a distance $r = \sigma$ and $\phi \rightarrow \infty$ as r becomes less than σ .

Under such conditions,
$$\int_0^{\infty} \left(1 - e^{\frac{-\phi}{kT}} \right) r^2 dr$$
$$= \int_0^{\sigma} \left(1 - e^{\frac{-\phi}{kT}} \right) r^2 dr + \int_{\sigma}^{\infty} \left(1 - e^{\frac{-\phi}{kT}} \right) r^2 dr$$

When $r < \sigma$, $\phi \rightarrow \infty$, $\therefore \int_0^{\sigma} \left(1 - e^{\frac{-\phi}{kT}} \right) r^2 dr = \int_0^{\sigma} r^2 dr$

So,
$$\int_0^{\infty} \left(1 - e^{\frac{-\phi}{kT}} \right) r^2 dr = \int_0^{\sigma} r^2 dr + \int_{\sigma}^{\infty} \left(1 - e^{\frac{-\phi}{kT}} \right) r^2 dr$$
$$= \frac{1}{3}\sigma^3 + \int_{\sigma}^{\infty} \frac{\phi}{kT} r^2 dr, \text{ since } \phi \rightarrow 0 \text{ as } r \gg \sigma$$

Therefore, equation (xi) may be written as,

$$PV = RT + \frac{2\pi N_0^2 kT}{V} \left[\frac{\sigma^3}{3} + \int_{\sigma}^{\infty} \frac{\phi}{kT} r^2 dr \right]$$
$$= RT + \frac{RT}{V} \left[\frac{2\pi N_0 \sigma^3}{3} + 2\pi N_0^2 \int_{\sigma}^{\infty} \frac{\phi}{RT} r^2 dr \right]$$
$$= RT + \frac{RT}{V} \left[b - \frac{a}{RT} \right]$$

where, $b = 2/3\pi N_0 \sigma^3$ and $a = -2\pi N_0^2 \int_{\sigma}^{\infty} \phi r^2 dr$.

The van der Waals equation is thus derived from the virial theorem, corrected upto the second term.

Re-writing equation (xi), we find

$$PV - \frac{2\pi N_0^2 kT}{V} \int_0^{\infty} \left(1 - e^{-\phi/kT} \right) r^2 dr = RT$$

or
$$\left[P + \frac{2\pi N_0^2 kT}{V^2} \int_0^{\infty} \left(e^{-\phi/kT} - 1 \right) r^2 dr \right] V = RT$$

Comparing this with van der Waals equation, we may approximately say that

$$a = 2\pi N_0^2 kT \int_0^\infty \left(e^{-\phi/kT} - 1 \right) r^2 dr$$

' a ' is a function of temperature and varies with the temperature, as has been stated earlier. Dependence of ' a ' on ϕ explains why it varies from gas to gas.

Comparing equation (xi) with K-onne's equation upto the second term, the second virial coefficient B may be given by

$$B = 2\pi N_0^2 kT \int_0^\infty \left(1 - e^{-\phi/kT} \right) r^2 dr$$

' B ' is also therefore a function of temperature.

The attractive forces between molecules are ascribed to several types of action. In molecules of many substances, there are electrical asymmetries. These lead to a positive centroid and a negative centroid with equal charges within the molecules rendering them polar. Such dipolar molecules orient and opposite ends attract one another. The interaction potential energy of attraction in a given substance (U') is shown to be inversely proportional to the sixth power of this distance, i.e.,

$U' = -\frac{A_1}{r^6}$, the negative sign indicating attraction (Keesom). The constant A_1 depends on the nature of the substance and the temperature.

The orientation is not the only cause of attraction. The polar molecules do induce a moment on the neighbouring molecules. This also gives rise to attractive forces between them. The potential energy resulting from this is given by $U'' = -\frac{A_2}{r^6}$, the constant A_2 depending upon temperature.

These explanations were not enough as the non-polar molecules like argon, oxygen, etc., also exhibit mutual attraction. It is now believed that the zero moment of a non-polar molecule is the resultant of a large number of instantaneous electrical arrangements, which are momentarily polar. Those fleeting polar configurations are able to induce moment to neighbouring similar members, in consequence of which the attraction takes place. Mathematically it has been shown

that the interaction energy of this nature will also be of the order, $U''' = -\frac{A^3}{r^6}$.

On the other hand, the repulsion is due to the interaction of the electron fields as the molecules approach one another. The interaction energy in repulsion is given by an expression of the form $U_r = +Br^{-m}$ where m varies from 9 to 15. When we consider both attraction and repulsion, a commonly used expression is

$$U = -Ar^{-6} + Br^{-12}$$

If the potential energies for attraction and repulsion be plotted against the intermolecular distances, the dotted curves as given in Fig. I.33 would be obtained. The full line curve shows the sum of the attractive and repulsive contributions. At large distances, potential energy is negative, i.e., attraction is predominant. The curve rises steeply, showing that repulsion exceeds the attraction and potential energy becomes positive. The point of intersection of the curve with the distance-axis gives the collision diameter, where attraction and repulsion balance each other.

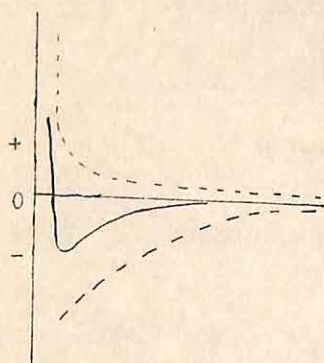


Fig. I.33

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I.29. Compressibility Factors. The constants 'a' and 'b' in the van der Waals equation depend on the nature of the gas. The equations therefore would be quantitatively different for different gases. The P - V - T relation for various gases cannot therefore be represented by the same curve. The same is true of other equations of state. The law of corresponding states, which is generally valid, however, enables us to obtain a generalised curve for different gases. The deviation of the real gases from the ideal states may be represented in the following manner :

$$PV = zRT \quad (\text{for 1 gm-mole})$$

where the factor z , called the *compressibility factor*, is a measure of the extent of deviation. Now, if we represent the P - V - T , in terms of critical quantities, we have

$$z = \frac{PV}{RT} = \frac{\pi P_c \times \phi V_c}{R\theta T_c} = \frac{P_c V_c}{RT_c} \cdot \frac{\pi \phi}{\theta}$$

The critical coefficient $\frac{P_c V_c}{RT_c}$ has been found experimentally to be a constant, though the magnitude may differ from those predicted by the different equations of state. We can then write

$$z = K' \cdot \frac{\pi \phi}{\theta}, \text{ where } K' = \text{universal constant.}$$

If the different gases are maintained at the same reduced temperature θ and then brought to the same reduced pressure π , their reduced molar volumes ϕ would be the same according to the law of corresponding states. Then, the value of z under such conditions for all gases would be the same. It is thus evident that if

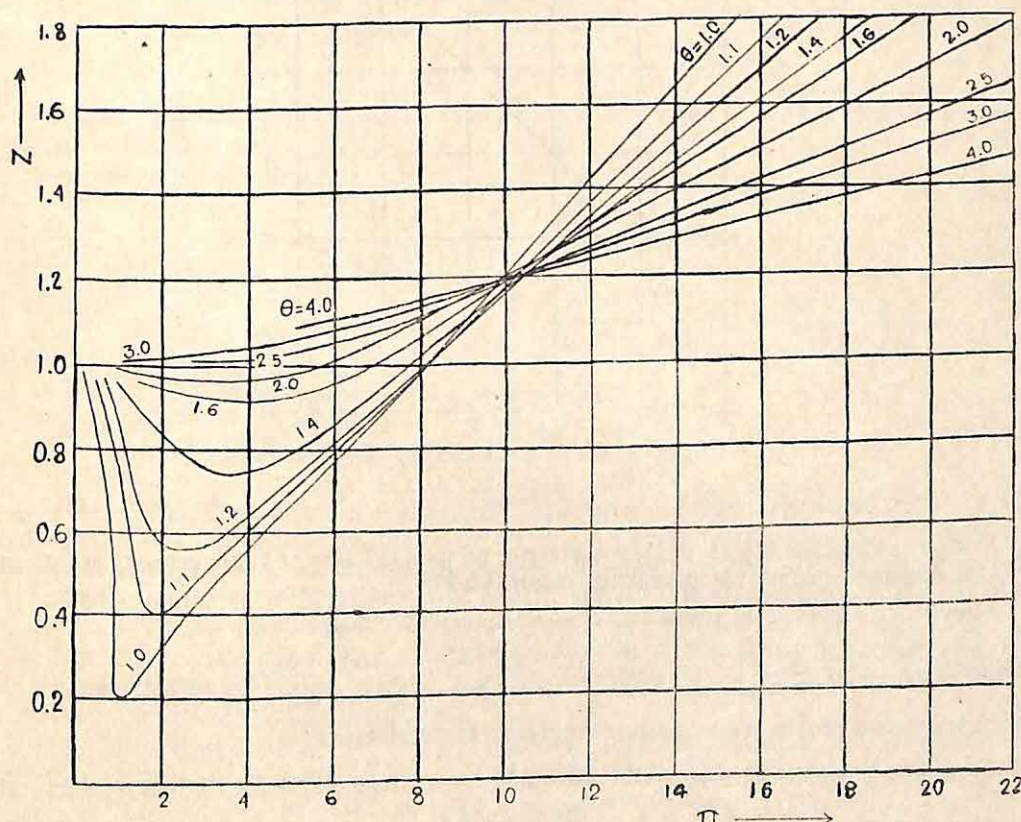


Fig. I.34

we plot z against π (at a given value of θ), the results will be identical for all gases. For any reduced temperature then we shall obtain a generalised curve (z versus π) which will be valid for all gases. In fact, experimentally this has been found to be

true. The mean compressibility factors have been derived and plotted against reduced pressures as shown in Fig. I.34. These curves may be conveniently employed to determine the pressure (or volume) of a real gas under different conditions.

Example : A gm-mole of ethylene ($T_c = 282.8^\circ K$, $P_c = 50$ atmos.) occupied a volume of 275 c.c. at $38^\circ C$. Calculate its pressure from the compressibility diagram.

$$\theta = \frac{T}{T_c} = \frac{273+38}{282.8} = 1.1$$

Now

$$\frac{zRT}{V} = \frac{0.082 \times 311}{0.275} z = 89.33z$$

And

$$\pi = \frac{P}{P_c} = \frac{89.33z}{50} = 1.79z$$

From Fig. I.34, the st-line $\pi = 1.79z$ cuts the compressibility diagram $\theta = 1.1$ at the point $z = 0.6$. (Fig. I.35)

Hence, the pressure $P = 89.33 \times 0.6 = 53.59$ atmospheres.

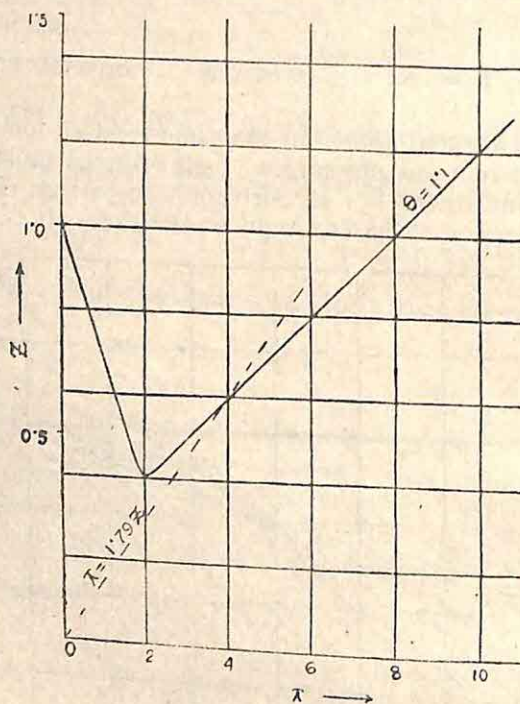


Fig. I.35

Problem : Calculate the wt. of O_2 necessary to fill up a cylinder of 5-litre capacity at $0^\circ C$ and 100 atm. pressure when the compressibility factor is 0.96.

Now

$$n = w/M \text{ gm-moles, } z = \text{compressibility factor}$$

Then

$$n = \frac{Pv}{zRT} \quad \text{or} \quad \text{wt. of } O_2 = \frac{PvM}{zRT} = \frac{100 \times 5 \times 32}{0.96 \times 0.082 \times 273} = 744.4 \text{ gms.}$$

A few typical problems on the equation of state are worked out here.

Problem : Calculate van der Waals' constants for ethylene. ($T_c = 282.8K$ and $P_c = 50$ atm.)

$$b = \frac{1}{8} \frac{RT_c}{P_c} = \frac{1}{8} \times \frac{0.082 \times 282.8}{50} = 0.057 \text{ litres.}$$

$$a = \frac{27}{64} R^2 \cdot \frac{T_c^2}{P_c} = \frac{27}{64} \times (0.082)^2 \times (282.8)^2 \times \frac{1}{50} = 4.47 \text{ litres}^2\text{-atmospheres.}$$

Problem : 100 gms of CO_2 are contained in a 5-litre globe at 40°C . Calculate its pressure (i) as a van der Waals gas, (ii) as an ideal gas. ($a = 3.59$, $b = 0.043$)

$$\text{Ideal : } P = \frac{nRT}{v} = \frac{100}{44 \times 5} \times 0.082 \times 313 = 11.67 \text{ atm.}$$

$$\begin{aligned} \text{van der Waals : } P &= \frac{nRT}{v-nb} - \frac{n^2a}{v^2} \\ &= \frac{100 \times 0.082 \times 313}{44 \left(5 - \frac{100}{44} \times 0.043 \right)} - \frac{\left(\frac{100}{44} \right)^2 \times 3.59}{25} \\ &= 11.16 \text{ atm.} \end{aligned}$$

Problem: Argon has ($T_c = -122^\circ\text{C}$, $P_c = 48 \text{ atm}$). What is the radius of the Argon atom?

$$\begin{aligned} b &= \frac{1}{8} \frac{RT_c}{P_c} = \frac{1}{8} \times \frac{0.082 \times 151}{48} \\ \therefore 4 \times \frac{4}{3} \pi r^3 \times N_0 &= b = \frac{1}{8} \times \frac{0.082 \times 151}{48} \text{ litres} \\ r &= \left[\frac{0.082 \times 151 \times 3 \times 10^3}{8 \times 48 \times 16 \times 3.14 \times 6 \times 10^{23}} \right]^{\frac{1}{3}} \text{ cms} \\ &= 1.47 \times 10^{-8} \text{ cms.} \end{aligned}$$

Problem : The second virial coefficient of an imperfect gas is 2×10^{-2} litres/mole. Calculate the volume of a gm-mole of the gas at 27°C and 5-atmospheres pressure.

$$PV = RT + BP \text{ (approx.)}$$

$$5 \times V = 0.082 \times 300 + 0.02 \times 5$$

or

$$V = 4.94 \text{ litres.}$$

Problem : Calculate the number of gms of hydrogen in a vessel of 500 c.c. capacity when the gas is forced in at 100 atm. at 127°C .

Using Berthelot equation,

$$P_v = nRT \left[1 + \frac{9}{128} \frac{P}{P_c} \cdot \frac{T_c}{T} \left(1 - \frac{6T_c^2}{T^2} \right) \right], \text{ we have}$$

$$100 \times \frac{1}{2} = n \times 0.082 \times 400 \left[1 + \frac{9}{128} \cdot \frac{100}{12.8} \times \frac{33.2}{400} \left(1 - \frac{6 \times 33.2^2}{400^2} \right) \right],$$

whence $n = 0.7 \text{ gm-moles} = 1.4 \text{ gms of hydrogen.}$

SEC. D—SOME SPECIAL PROPERTIES OF GASES

1.30. The Heat Capacity of Gases. The quantity of heat required to raise the temperature of the body by one degree is called its heat-capacity. Usually the rise in temperature is measured in centigrade degrees and the heat-capacity is expressed in calories. Obviously, the heat capacity will depend upon the amount of the material in the system. If the amount of the substance is one gram, the heat-capacity is the same as the *specific heat*. But commonly in chemistry, the amount is expressed in gm-moles. The heat-capacity of a gm-mole of the substance is called the *molar heat capacity*.

The magnitude of heat-capacity depends on the pressure and the volume, specially in the case of gases. Thus, if the temperature of a gm-mole of gas is raised by 1°C keeping it at constant volume and again in another operation the same rise of temperature is made allowing the volume to vary, the quantities of heat necessary in the two cases would be different. Hence, in mentioning the heat capacity of a gas, the conditions have to be specified. Two standard conditions are usually followed, (i) the heat capacity at constant volume denoted by C_v and (ii) the heat-capacity at constant pressure denoted by C_p .

Let us first consider the monatomic gases like Argon, Helium, etc. If such a gas be heated at *constant volume*, the heat supplied will be entirely utilised in increasing the kinetic energy of translation of the molecules. Since the molecules are monatomic, there cannot be any absorption in vibrational or rotational motion, and further, volume remaining constant, no energy can be used to do any mechanical work of expansion. We know, for a gm-mole of the gas, the kinetic energy, at temperature T , is

$$E = \frac{3}{2}PV = \frac{3}{2}RT.$$

The increase in kinetic energy for 1° rise in temperature,

$$\Delta E = \frac{3}{2}R[(T+1)-T] = \frac{3}{2}R \approx 3 \text{ calories.}$$

The heat supplied at constant volume is equal to the rise in kinetic energy, hence

$$C_v = \Delta E = 3 \text{ calories (for a monatomic gas)}$$

The experimental results have confirmed the same.

But if the monatomic gas be heated at constant pressure the gas expands against the piston (Fig. I.36) and does mechanical work. In order to attain 1° rise in temperature, the heat supplied should be sufficient to provide the kinetic energy (ΔE) to the molecules and also to enable to do the extra mechanical work. If V_2 and V_1 be the final and initial volumes of the gas at constant pressure P , the work done

$$\omega = P(V_2 - V_1) = R(T_2 - T_1) = R \approx 2 \text{ calories.}$$

Hence the total heat to be supplied to 1 mole of gas at constant pressure,

$$C_p = \Delta E + \omega = C_v + R$$

Hence, for a mole of monatomic gas, the difference of heat capacities at constant pressure and volume, is given by

$$C_p - C_v = 2 \text{ calories.} \quad \dots (I.62)$$

The ratio of the two heat-capacities, universally expressed by the symbol γ is,

$$\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} \approx \frac{5}{3} = 1.66 \quad \dots (I.63)$$

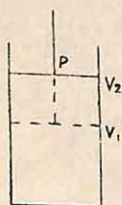


Fig. I.36

for a monatomic gas. The experimental data are in complete harmony with the relation as shown in the Table below.

For polyatomic molecules, the heat supplied is used up not only in augmenting the translational kinetic energy but also in increasing the vibrational and rotational energies. If x calories be used for the latter purposes, then,

$$C_v = \Delta E + x = \frac{3}{2}R + x = 3 + x.$$

$$C_p = \Delta E + \omega + x = \frac{3}{2}R + R + x = 5 + x$$

Hence, the heat-capacity-difference remains the same, two calories, as in monatomic gases, but the heat-capacity-ratio (γ),

$$\gamma = \frac{C_p}{C_v} = \frac{5+x}{3+x}$$

The value of γ would be less than 1.66 and its lower limit is 1.0. As the complexity of the molecule increases, the value of x becomes larger and larger and the ratio γ diminishes. Usually for diatomic molecules $\gamma = 1.40$, for triatomic molecules $\gamma = 1.31$ and so on. In the table below are given the heat-capacities of some common gases.

MOLAR HEAT CAPACITIES IN CALORIES

(P = 1 atm., T = 298°K)

Gas	C_p	C_v	γ
Argon	4.97	2.98	1.66
Helium	4.97	2.98	1.66
Mercury	5.0	3.5	1.67
Hydrogen	6.85	4.86	1.40
Nitrogen	6.96	4.97	1.40
Oxygen	7.03	5.03	1.40
Chlorine	8.10	6.00	1.35
Nitric Oxide	7.10	5.10	1.39
Carbon dioxide	8.83	6.80	1.30
Sulphur dioxide	9.65	7.50	1.29
Nitrous oxide	9.08	7.03	1.29
Water	8.67	6.47	1.34
Methane	8.50	6.50	1.31
Acetylene	10.45	8.40	1.24
Ethane	10.25	8.20	1.25

The heat capacities C_p and C_v for polyatomic gases are also found to vary with temperature. From experimental data, several empirical relations between heat-capacity and temperature have been developed. Usually both C_p and C_v increase with temperature. The commonly used relations are

$$C_p = a + bT + cT^2 + \dots \quad \dots (I.64)$$

where $a, b, c, \dots$ are constants,

$$\text{and} \quad C_v = a_1 + b_1 T \quad \dots (I.65)$$

$$\text{i.e.,} \quad \frac{\partial C_v}{\partial T} = b_1$$

In the table below are given the C_p -values of some common gases and vapours.

 HEAT CAPACITIES OF DIFFERENT GASES AT CONSTANT
 PRESSURE IN THE TEMPERATURE RANGE 300°–1500°

Gas	a	$b \times 10^8$	$c \times 10^7$
H ₂	6.95	0.19	+ 4.8
O ₂	6.15	3.1	— 9.23
N ₂	6.52	1.25	— 0.01
H ₂ O	7.25	2.29	+ 2.83
CO ₂	6.21	10.4	—
CH ₄	3.38	18.0	— 43.0
C ₂ H ₆	2.24	38.2	— 110.4
C ₆ H ₆	— 0.41	77.6	— 264.3

For the determination of the heat-capacities and also the heat-capacity ratio, different methods have been employed. It would be useful to discuss the outline of a few of these methods here.

Determination of C_v . The heat-capacity at constant volume is often measured by using Joly's steam calorimeter (Fig. I.37)*. Two identical thin-walled copper spheres are suspended at the two ends of a balance beam. The spheres are enclosed in a chamber into which steam can be let in. The two spheres exactly balance one another. When steam is introduced into the cham-

* Ref : Proc. Roy. Soc. 47, 218, 1889

ber, equal amounts of it condense on the two spheres and the balance is maintained. Now for this experiment one sphere is completely evacuated and the other is filled up with the experimental gas. On admitting steam, it is now found that more water condenses on the sphere which contains the gas. The difference is found by adding wts. to the other pan. The difference in the amount of

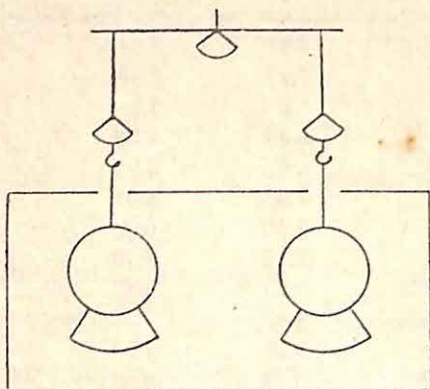


Fig. I.37

steam condensed is due to the different heat-capacities of the spheres. It is easy to calculate now the heat-capacity of the gas. If w gms of steam be the excess amount condensed and x gm-moles of the gas (molar heat-capacity, C_p) be taken in the sphere, then

$wL = xC_p(T_2 - T_1)$, where T_2, T_1 , are the final and initial temperatures of the spheres and L is the latent heat of steam. C_p is thus known.

Determination of C_p . The heat-capacity at constant pressure may be determined by the Mccollum's method*. The gas under investigation is allowed first to flow through a long spiral coil kept immersed in a constant temperature bath at a uniform but slow speed. The gas in passing through the long coil attains the temperature of the bath (T_1). The gas next enters into a second coil immersed in another bath which is at a slightly higher temperature (T_2) maintained with the help of an electrical heater. As the gas enters into the second bath, the temperature of the bath

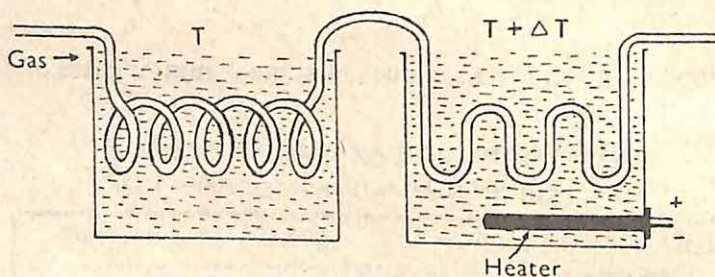


Fig. I.38

tends to fall as the comparatively colder gas absorbs some heat. But the loss of heat is compensated by supplying extra-current to the heater. This additional current required to maintain constant temperature is measured. A diagrammatic sketch of the Mccollum's method is given in Fig. I.38. Now if x moles of gas of heat capacity C_p pass through the spiral per second and if I denotes the additional current, the resistance of the heater being r , then

$$xC_p(T_2 - T_1) = \frac{I^2 r}{4.2}$$

or

$$C_p = \frac{I^2 r}{4.2 \times x \times (T_2 - T_1)}$$

Determination of γ . The determination of γ , the ratio of heat capacities, is based on two different methods ; (i) the study of the adiabatic expansion of the gas, or (ii) the measurement of the velocity of sound in the gas.

Method depending on adiabatic change : An adiabatic change is one in which no heat is allowed to enter into, or escape from, the system during the change, i.e., heat-transfer between the system and the surroundings is not permitted. It

* Mccollum : J. Am. Ch. Soc. 44, 28, 1927.

will be seen later (Chap. IV) that if under such adiabatic condition a gas is allowed to expand, the P - v relation will be represented as

$$Pv^\gamma = \text{constant},$$

where γ is the heat-capacity ratio.

This relation was utilised by Clement and Desormes for the first time to find out γ . A very large vessel provided with a stopcock was filled up with the gas at a pressure somewhat higher than that of the external atmosphere. The pressure was noted from an attached manometer. The stopcock was opened for a short while, when the gas expands and a portion goes out. The change is sudden and adiabatic. The pressure inside falls to that of the external atmosphere. Due to expansion, the gas also cools. The stop cock is then closed. The gas now slowly attains the original temperature and consequently the pressure also increases.

Suppose the original pressure of the gas is P_1 and the atmospheric pressure is P . If V_1 and V denote the volumes of a gm-mole of the gas at pressures P_1 and P respectively, then for the adiabatic expansion, we have,

$$P_1 V_1^\gamma = P V^\gamma \quad \dots (i)$$

Let the final pressure of the gas be P_2 (when the original temperature is also attained). Then, according to Boyle's Law, for one mole of gas,

$$P_2 V = P_1 V_1 \quad \dots (ii)$$

Eliminating V and V_1 we have,

$$\left(\frac{P_1}{P}\right)^{\frac{1}{\gamma}} = \frac{P_1}{P_2}$$

or

$$\gamma = \frac{\log P_1 - \log P}{\log P_1 - \log P_2} \quad \dots (1.66)$$

The value of γ is thus known from the manometer readings.

Lummer and Pringsheim and, later on, Partington considerably improved the method in which they measured the drop in temperature after adiabatic expansion. A large copper globe (130 litres capacity) provided with a manometer and a controlled valve was used. The temperature was measured accurately from the resistance variation of a thin Pt -wire kept inserted in the globe (Fig. I.39).

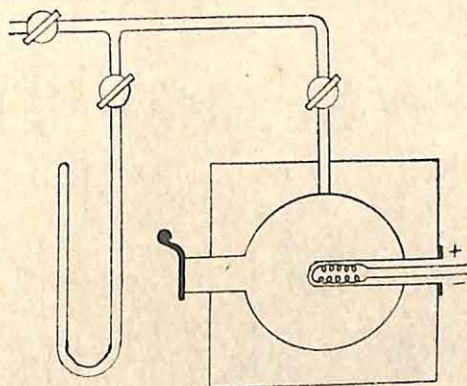


Fig. I.39

Suppose initially the temperature is T_1 , pressure P_1 and molar volume V_1 . On adiabatic expansion, the pressure falls to P , temperature to T and the molar volume becomes V . Then, for the adiabatic expansion of the gas,

$$P_1 V_1^\gamma = P V^\gamma \quad \dots (iii)$$

Also,

$$P_1 V_1 = RT_1 \text{ and } P V = RT \quad \dots (iv)$$

i.e.,

$$\frac{V_1}{V} = \frac{T_1 P}{T P_1}$$

Again from (iii),
$$\frac{V_1}{V} = \left(\frac{P}{P_1} \right)^{\frac{1}{\gamma}}$$

$$\therefore \frac{T_1}{T} \cdot \frac{P}{P_1} = \left(\frac{P}{P_1} \right)^{\frac{1}{\gamma}}$$

or
$$\gamma = \frac{\log P_1 - \log P}{(\log P_1 - \log P) - (\log T_1 - \log T)} \quad \dots (1.67)$$

The value of γ is thus known.

Method depending on the velocity of sound : The velocity of sound V is given by the relation

$$V^2 = \gamma \left(\frac{\partial P}{\partial \rho} \right)_T \quad \dots (1.68)$$

where ρ is the density of the gas. A measurement of V will thus enable us to compute the value of γ . Dixon used a long coiled tube (15 metres), closed at each end by a diaphragm. A hammer was used to strike the diaphragm and produce the sound wave. Two thin platinum discs are inserted inside the tube near the two ends and are so adjusted that when the wave passes them, a self-recording chronometer is started (Fig. I.40). It is thus possible to measure the time the sound-wave takes to cover the length of the tube. Hence the velocity V is known.

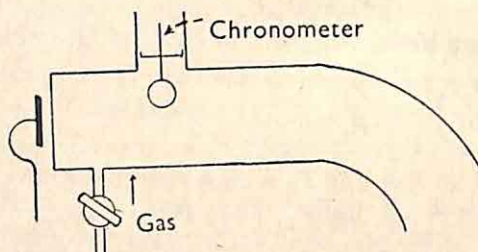


Fig. I.40

Now

$$\gamma = V^2 \left(\frac{\partial \rho}{\partial P} \right)_T$$

If we take the gas as a perfect one, then, $\gamma = V^2 \frac{M}{RT}$. But for the real gases often Berthelot's equation is used. So,

$$\begin{aligned} \rho &= \frac{M}{v} \approx \frac{M}{RT} \left[1 + \frac{9}{128} \frac{PT_c}{TP_c} \left(1 - \frac{6T_c^2}{T^2} \right) \right]^{-1} \\ &= \frac{MP}{RT} \left[1 - \frac{9}{128} \frac{PT_c}{TP_c} \left(1 - \frac{6T_c^2}{T^2} \right) \right] \end{aligned}$$

Hence
$$\left(\frac{\partial \rho}{\partial P} \right) = \frac{M}{RT} \left[1 - \frac{9}{64} \frac{PT_c}{TP_c} \left(1 - \frac{6T_c^2}{T^2} \right) \right]$$

$$\therefore \gamma = V^2 \frac{M}{RT} \left[1 - \frac{9}{64} \frac{PT_c}{TP_c} \left(1 - \frac{6T_c^2}{T^2} \right) \right] \quad \dots (1.69)$$

I.31. The Principle of Equipartition of Energy and the Heat Capacity of Gases. The average translational kinetic energy of a gm-mole of gas is

$$E_{tr} = \frac{1}{2} m N_0 \bar{c}^2 = \frac{3}{2} RT.$$

This translational energy depends only on the temperature and is independent of the mass and nature of the molecules. It is also known that the mean squares of c_x , c_y , c_z , the components of the velocity c in three mutually perpendicular directions are equal (Sec. I.7), i.e.,

$$\overline{c_x^2} = \overline{c_y^2} = \overline{c_z^2} = \frac{1}{3} \bar{c}^2$$

It leads to the conclusion that molar translational energy ($\frac{3}{2}RT$) is made up of three equal parts corresponding to velocities along three axes at right angles. In each direction, the average kinetic energy of translation per mole is $\frac{1}{2}RT$. Hence,

for each molecule the average translational energy is $\frac{1}{2} \frac{RT}{N_0} = \frac{1}{2}kT$ in each direction. For translational motion, each molecule is said to have three degrees of freedom, each of which contributes an energy $\frac{1}{2}kT$ towards the total translational energy. By the expression "degrees of freedom" is meant the possible modes or directions of motion. The translational motion of every molecule can be resolved into three possible directions, i.e., every molecule has always three translational "degrees of freedom", each degree of freedom contributing $\frac{1}{2}kT$ of energy. Again, the translational energy along the three degrees of freedom is given by $\frac{1}{2}mc_x^2$, $\frac{1}{2}mc_y^2$ and $\frac{1}{2}mc_z^2$. Hence for each degree of freedom, the translational energy is expressed by a quadratic term. Alternatively, "degrees of freedom" constitute the number of quadratic terms required to express the total energy of the molecule. In the case of a monatomic gas like argon, neon, etc., there is only the translational energy and hence only three degrees of freedom. For diatomic and polyatomic molecules there are, in addition, rotational and vibrational motions and hence the degrees of freedom would be larger.

That the average kinetic energy of translation along each direction would be $\frac{1}{2}kT$ is a consequence of the Maxwell distribution law. It is true that the average value of the velocity component along a direction would be zero, for the number of molecules having velocity components c_x and $-c_x$ would be equal. But the average energy in respect of that component would be a positive quantity, $\frac{1}{2}mc_x^2$ and $\frac{1}{2}m(-c_x)^2$. With Maxwell distribution, we may calculate the average energy, $\bar{\epsilon}_x$. From Sec. I.14 (ix), we have

$$\begin{aligned}\bar{\epsilon}_x &= \frac{1}{n} \int \int \int \frac{1}{2} mc_x^2 \cdot dn_{c_x, c_y, c_z} \\ &= \frac{1}{n} \int \int \int \frac{1}{2} mc_x^2 n A^3 e^{-b(c_x^2 + c_y^2 + c_z^2)} dc_x \cdot dc_y \cdot dc_z \\ &= \frac{1}{2} mA^3 \int_{-\infty}^{\infty} c_x^2 e^{-bc_x^2} dc_x \int_{-\infty}^{\infty} e^{-bc_y^2} dc_y \int_{-\infty}^{\infty} e^{-bc_z^2} dc_z.\end{aligned}$$

(since the energy may have any value).

Substituting the values of the integrals (Appendix 1.3)

$$\begin{aligned}\bar{\epsilon}_x &= \frac{1}{2} mA^3 \cdot \left[\frac{1}{2} \frac{\pi^{\frac{1}{2}}}{b^{\frac{3}{2}}} \right] \left[\frac{\pi}{b} \right]^{\frac{1}{2}} \left[\frac{\pi}{b} \right]^{\frac{1}{2}} \\ &= \frac{1}{4} mA^3 \cdot \frac{\pi^{\frac{3}{2}}}{b^{\frac{5}{2}}}\end{aligned}$$

Since $A = \sqrt{\frac{b}{\pi}}$ and $b = \frac{m}{2kT}$, the expression easily reduces to

$$\bar{\epsilon}_x = \frac{1}{2}kT$$

Similarly, $\bar{\epsilon}_y = \frac{1}{2}kT$, and $\bar{\epsilon}_z = \frac{1}{2}kT$

$$\therefore \epsilon_{tr} = \bar{\epsilon}_x + \bar{\epsilon}_y + \bar{\epsilon}_z = 3 \times \frac{1}{2}kT = \frac{3}{2}kT$$

By an extension of the distribution law, Maxwell and Boltzmann enunciated that

"The total kinetic energy of a molecule is equally distributed between the various degrees of freedom."

This is known as the principle of equipartition of energy. We have just found that every translational degree of freedom contributes an energy $\frac{1}{2}kT$. According to the principle, each of all other possible degrees of freedom would be associated with an energy $\frac{1}{2}kT$. If there be altogether γ degrees of freedom, the net kinetic energy of the molecule would amount to $\frac{1}{2}\gamma kT$.

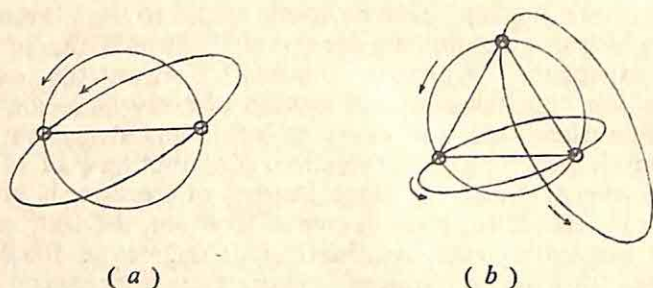


Fig. I.41

To illustrate : A diatomic molecule has translational, rotational and vibrational energy. For translatory motion there are 3 degrees of freedom. For its rotational motion, the two atoms may be considered as a dumbbell, rotating along two axes at right angles [Fig. I.41 (a)]. The rotational energies are $\frac{1}{2}I\omega_1^2$, and $\frac{1}{2}I\omega_2^2$ where ω_1, ω_2 are angular velocities and I_1, I_2 are moments of inertia. That is, there are two quadratic terms for energy for the two modes of rotation. That is, there are two rotational degrees of freedom for a diatomic molecule, so that $\epsilon_{rot} = 2 \times \frac{1}{2}kT = kT$. As for the vibrational motion, the two atoms oscillate against one another so that the molecule possesses both kinetic and potential energy. The kinetic energy is $\frac{1}{2}mu^2$ and the potential energy $\frac{1}{2}\mu r^2$ (μ , the force constant and r , the inter-atomic distance). It means that the energy for vibration involves two quadratic terms or two degrees of freedom. Each vibration type of motion in a molecule will thus be associated with $2 \times \frac{1}{2}kT$ energy. For a diatomic molecule then, the total energy of the molecule

$$\epsilon = \epsilon_{tr} + \epsilon_{rot} + \epsilon_{vib} = 3 \times \frac{1}{2}kT + 2 \times \frac{1}{2}kT + 2 \times \frac{1}{2}kT = \frac{7}{2}kT$$

For a mole of diatomic gas, $E = \frac{7}{2}RT$.

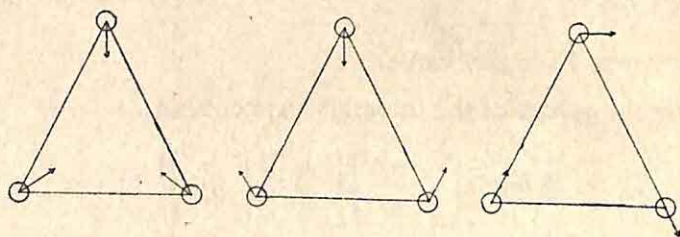


Fig. I.42

In the case of a triatomic molecule (nonlinear), there will be three translational and three rotational degrees of freedom [Fig. I.41(b)]. Besides, there shall be also three types of vibration (Fig. I.42), each type involving an energy ($2 \times \frac{1}{2}kT$). Hence in a non-linear triatomic molecule, the energy will be

$$\epsilon = 3 \times \frac{1}{2}kT + 3 \times \frac{1}{2}kT + 3 \times (2 \times \frac{1}{2}kT) = 6kT.$$

For a gm-mole,

$$E = 6RT.$$

In general, for a polyatomic molecule of n atoms, there are three degrees of freedom for translation and three for rotation ; the types of vibration are $(3n-6)$, the number of squared terms for vibration is $2(3n-6)$. If the polyatomic molecule be linear, the rotational degrees of freedom shall be 2 and the vibrational $2(3n-5)$. Thus if r and v denote the degrees of freedom for rotation and vibration, then the total molar energy, according to the principle of equipartition will be

$$E = (3+r+v) \times \frac{1}{2}RT.$$

Hence the heat-capacity at constant volume

$$C_v = \frac{\partial E}{\partial T} = (3+r+v)\frac{1}{2}R.$$

The heat capacity at constant pressure, $C_p = (3+r+v)\frac{1}{2}R + R = (5+r+v)\frac{1}{2}R$.

or, the heat capacity ratio, $\gamma = \frac{C_p}{C_v} = \frac{5+r+v}{3+r+v}$.

Some of the experimental results of heat-capacities at different temperatures are given in the table below.

C_v FOR GASES

Gas	Temperature (°C)			
	0°	100°	200°	600°
He	2.98	2.98	2.98	2.98
A	2.98	2.98	2.98	2.98
Hg	2.98	3.00	3.00	3.00
O ₂	5.00	5.15	5.60	6.19
N ₂	4.95	4.96	5.15	5.26
Cl ₂	5.85	5.88	6.24	6.80
CO ₂	6.68	7.68	8.30	10.90

For the monatomic gases, the experimental results agree well with the theoretically predicted value $3 \times \frac{1}{2}R = 2.97$ calories. For diatomic gases, the equipartition principle predicts the value $7/2R = 6.94$ calories. This is reached only at high temperatures but at lower ranges of temperature the observed C_v -values are much less. For polyatomic gases, the departure from theoretically calculated values is still higher. The principle of equipartition is thus inadequate to explain either the variation of heat-capacity for different diatomic gases or the rise in C_v -values with increase in temperature. The principle however explains the absorption along translational degrees of freedom. There is a limitation on the appearance of equipartition at lower temperatures in respect of vibration and rotation. The principle of equipartition is derived from the classical considerations of continuous absorption of energy governed by Maxwell distribution. But in vibration and rotation, we now know, the absorption of energy takes places in discrete quantities. The observed results can therefore be explained only on the basis of quantum theory. At high temperatures when energy levels are quite close and the distribution would be practically continuous, the principle would be valid.

DENSITY OF GASES AND VAPOURS : MOLECULAR WEIGHTS

The density of a gas or vapour is the mass per unit volume at a given temperature and pressure. The standard density or normal density is the density at 0°C and 1 atmosphere pressure. In calculations of molecular weights, relative densities referred to oxygen are used. Thus the gas density is the ratio of the masses of equal volumes of the gas and of oxygen, the latter being taken as 16, under the same conditions of temperature and pressure. The importance of determination of the gas or vapour density lies in the evaluation of molecular and atomic weights. The methods used for the determination of gas density and of vapour density are somewhat different and these are therefore treated here separately.

I.32 Gas Density. The oldest and yet sufficiently accurate method of determining the density of a gas is to weigh the same in a comparatively large globe of known volume (Regnault). Various corrections are to be made for errors due to buoyancy, moisture condensation on the surface, etc. Lord Rayleigh determined the density of nitrogen by this method in his historic experiments of the discovery of inert gases.

In the 'volumeter' method (Guye), globes are filled with the gas at a definite temperature and the pressure is measured from the attached manometer. The gas is then pumped out and absorbed in a suitable absorbent. The increase in the

weight of the absorbent gives the quantity of the gas, while its pressure is obtained from the initial and final readings of the manometer. The density then can be easily calculated.

Buoyancy Microbalance method : From the beginning of this century, buoyancy microbalance has been used for the determination of gas density wherever high degree of accuracy is required and specially when the quantity of the gas is small.

The microbalance used by Whytlaw-Gray in the determination of the density of radon (Fig. 1.43) consisted of an evacuated quartz buoyancy globe (8 c.c.) X, suspended at one end of a quartz beam Z. This was counterbalanced by a thin sheet of quartz Y, at the other end of the beam, the surface areas of the globe and the sheet being almost equal. The beam was suspended from a frame by a stretched quartz fibre T. The whole thing was enclosed inside a container of about 10 cms length kept at a constant temperature (say 0°C) and provided with a manometer. The container is first evacuated and the gas is then slowly introduced until a pointer at the end of Y points to a fixed zero mark O. The pressure P_1 is noted. The experiment is then repeated with pure oxygen gas and the corresponding pressure P_2 is also determined.

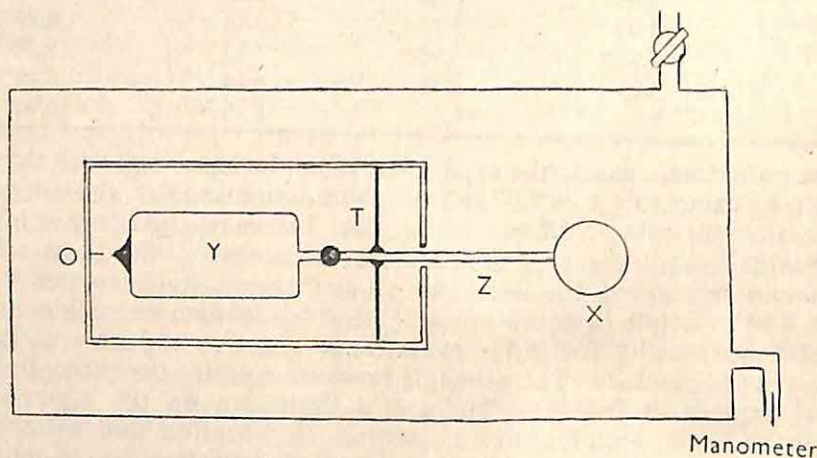


Fig. 1.43

It is easily seen that whenever the globe would counterbalance the quartz sheet, the density of the gas introduced must be the same. For, suppose the volume of the globe = V and the volume of the sheet = V' and the true wt. of the globe = w and the true weight of the sheet = w' . Then if d be the density of the gas in which these are balanced, we have, since the buoyancy effects are equal,

$$w - Vd = w' - V'd, \text{ or } d = \frac{w - w'}{V - V'}$$

Since the w , w' and V , V' are all fixed, the density must be the same when these balance one another.

Now suppose in this experiment ρ_2 is the density of oxygen under pressure P_2 and ρ_1 is the density of the gas taken under pressure P_1 . Then $\rho_1 = \rho_2$.

But we also know, $\rho_1 = \frac{P_1 M_1}{RT}$ and $\rho_2 = \frac{P_2 M_2}{RT}$ where M_1 = molecular wt. of the gas and M_2 = mol. wt. of oxygen.

Then
$$\rho_1 = \rho_2 = \frac{P_2 \times 32}{RT}, \text{ i.e., } \rho_1 \text{ is known.}$$

Let ρ_0 be the normal density of the gas under pressure P_0 (1 atm.).

$$\frac{\rho_0}{\rho_1} = \frac{P_0}{P_1}, \text{ or } \rho_0 = \rho_1 \cdot \frac{P_0}{P_1} \quad \dots (i)$$

Hence, the normal density of the gas is known

We can also write $\rho_0 = \frac{P_1 M_1}{RT} = \frac{P_2 M_2}{RT}$, since $\rho_1 = \rho_2$.

$$\text{or} \quad M_1 = \frac{P_2}{P_1} \cdot M_2 = 32 \frac{P_2}{P_1}$$

That is, the molecular weight can also be directly found out. The density of the gas at different pressures can be measured by replacing the quartz globe with others having different weights.

I.33. Limiting Densities. In determining the normal density ρ_s we have used the ideal gas equations which are not valid for real gases. It is therefore necessary to make adequate corrections for the results obtained. It may be clearly understood in the following way. Suppose ω gms of a gas are taken in each experiment and let $V_1, V_2, V_3, \dots$ be the volumes occupied by the same under pressures $P_1, P_2, P_3, \dots$

..... etc. Then, the densities at the respective pressures are $\frac{\omega}{V_1}, \frac{\omega}{V_2}, \frac{\omega}{V_3}, \dots$ etc. The

normal density (under unit pressure) will be $\frac{\omega}{P_1 V_1}, \frac{\omega}{P_2 V_2}, \frac{\omega}{P_3 V_3}, \dots$. Since

Boyle's Law is not obeyed, (i.e., PV -value is not constant) the magnitudes of the normal density would differ and would obviously be inaccurate. The truly accurate value would be the one measured under conditions where Boyle's Law is valid. This is possible at extremely low pressures or zero pressure (P_0) (where $\text{Lt } P \rightarrow 0$), when the volume V_0 is enormously large. The normal density will then

be $\frac{\omega}{P_0 V_0}$. It is the accurate normal density obtained from the limiting values of PV , and is hence termed the *limiting density*, ρ_0 . We have, normal density,

$$\rho_s = \frac{\omega}{P_1 V_1} \text{ and the limiting density, } \rho_0 = \frac{\omega}{P_0 V_0}$$

$$\text{i.e.,} \quad \rho_0 = \rho_s \cdot \frac{P_1 V_1}{P_0 V_0}$$

$$\text{or} \quad \text{Limiting density} = \text{normal density} \times \frac{P_1 V_1}{P_0 V_0} \quad \dots (ii)$$

The observed normal density should be corrected by multiplying with the factor $\frac{P_1 V_1}{P_0 V_0}$. Different indirect methods are used to determine this factor as direct measurement of $P_0 V_0$ is not possible.

(a) For gases having a relatively low compressibility, it has been found that the product PV at low pressures (below one atmosphere) bears a linear relationship to the pressure P . The experimental PV -values measured at several low pressures are plotted against P . The st-line obtained is extrapolated to cut the PV -axis to obtain the point $P_0 V_0$ ($\text{Lt } P \rightarrow 0$). Substituting this in equation (ii) above, the limiting density can be evaluated.

(b) For compressible gases, the relative deviation of the PV -values at low pressures is found to be directly proportional to the pressure P . The relative deviation is $\frac{P_0 V_0 - P_1 V_1}{P_1 V_1}$. Hence, at any low pressure, P_1 ,

$$\frac{P_0 V_0 - P_1 V_1}{P_1 V_1} = \lambda P_1 \quad \dots (iii)$$

The constant λ is called the compressibility coefficient. Rewriting,

$$P_0 V_0 = P_1 V_1 (1 + \lambda P_1)$$

Measurement of PV at two low pressures P_x and P_y will enable us to determine the quantity λ .

$$P_0 V_0 = P_x V_x (1 + \lambda P_x) = P_y V_y (1 + \lambda P_y)$$

Again, when $P = P_1 = 1$ atmosphere, $P_0 V_0 = P_1 V_1 (1 + \lambda)$

$$\text{or} \quad \frac{P_1 V_1}{P_0 V_0} = \frac{1}{1 + \lambda}$$

Hence, limiting density, $\rho_0 = \rho_s \cdot \frac{1}{1 + \lambda}$

As λ is known, the limiting density can be easily found out.

(c) Suitable equations of state can also be utilised to find out the factor $\frac{P_1 V_1}{P_0 V_0}$.

Thus, using Berthelot's equation, we can write

$$\frac{P_1 V_1}{P_0 V_0} = \frac{P_1 V_1}{RT} = 1 + \frac{9}{128} \cdot \frac{P_1 T_c}{TP_c} \cdot \left(1 - \frac{6T_c^2}{T^2} \right)$$

$$\text{Or we may say,} \quad \frac{1}{1 + \lambda} = 1 + \frac{9}{128} \frac{P_1 T_c}{TP_c} \left(1 - \frac{6T_c^2}{T^2} \right)$$

The knowledge of the critical constants would enable us to calculate the required factor to obtain the limiting density.

I.34. Vapour Density : (i) *Dumas method.* This method is based on the determination of the weight of a known volume of the vapour. In a comparatively large bulb with a narrow mouth is taken a little quantity of the liquid. The bulb is then placed in a constant high-temperature bath, when the liquid inside boils. When the whole liquid has vaporised and the bulb is filled up with vapour, the mouth of the bulb is sealed. The bulb is next taken out, cooled and weighed. The volume of the bulb and weight of the bulb alone are predetermined by weighing the bulb full of air and filled up with water. The temperature of the bath and atmospheric pressure are also noted. It is easy to obtain the density of the vapour from these observations (Fig. I.44).

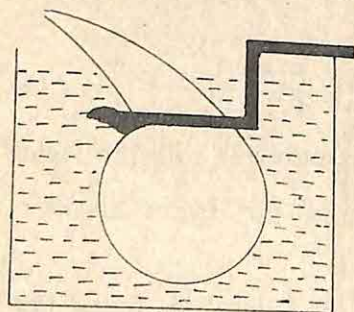


Fig. I.44. Dumas apparatus for vapour density determination

(b) *Hofmann's method.* In this method a known weight of the liquid is introduced into the vacuum over mercury in a barometer at a temperature higher than the *b.pt.* of the liquid. The barometer is surrounded by a jacket through which the vapour of a higher boiling liquid is passed to maintain the barometer at a sufficiently high and constant temperature. In Fig. (I.45) is given an outline of the arrangement. In a small Hofmann bottle a small quantity

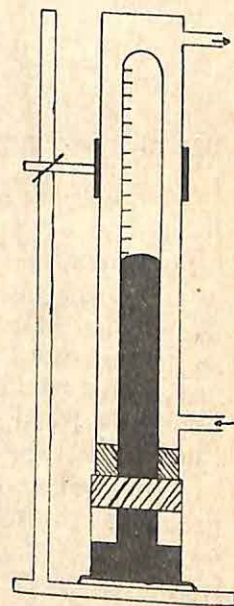


Fig. I.45. Hofmann's apparatus for determination of vapour density

of liquid (of known weight) is introduced into the barometer tube. The bottle goes to the top of the mercury column and the liquid vaporizes depressing the mercury column. The volume of the vapour is directly read from the scale, the depression gives the pressure and the temperature is also noted. The normal vapour density may be easily obtained.

(c) *Victor Meyer's Method.* For its simplicity and convenience of operation, this method is most frequently used. The principle involved is that the vapour produced from a known weight of the liquid is allowed to displace an equal volume of air, which is collected and measured at room temperature and pressure.

One form of the apparatus is shown in Fig. I.46. A long tube (about 1 cm diameter) ending in an elongated bulb at the bottom and having a capillary side tube at the top is used for vaporizing the liquid. This vaporization tube is often called Victor Meyer's tube. It is surrounded by a glass or copper jacket containing a liquid which boils at a temperature 20° or 25° higher than the boiling pt. of the experimental substance and maintains a constant temperature for the inner tube. The open mouth of the vaporization tube is closed by means of a rubber cork and the outer end of the side-tube is kept immersed in a trough of water. The liquid in the outer jacket is allowed to boil sufficiently long so that the steady condition is reached. This is indicated by the cessation of bubbles coming out through the capillary tube. A graduated measuring tube filled with water is now kept inverted over the end of the capillary tube.

A minute bulb or a small Hofmann bottle containing a known amount of the experimental liquid (about 0.15 gms), is then dropped into the vaporization tube by momentarily removing the rubber cork from its mouth. As soon as the bottle reaches the bottom of the Victor Meyer tube, the liquid vaporizes and pushes out an *equal volume of air* through the capillary side-tube to the graduated measuring tube. The graduated tube containing the collected air is then partly immersed in the same inverted manner into a tall jar of water such that water levels inside and outside are the same. The volume of the moist air under the atmospheric pressure is noted and also the temperature of the water. The atmospheric pressure is ascertained from the barometric reading. The vapour density may now be calculated in the following way.

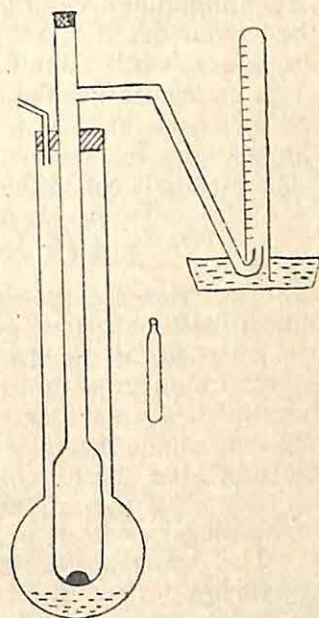


Fig. I.46

Suppose	Weight of the liquid taken	= g gms.
	Volume of the moist air collected	= v c.c.
	Barometric height	= P mm.
	Temperature	= $t^\circ\text{C}$
	Aqueous tension at $t^\circ\text{C}$	= f mm.

Let v_0 be the volume of the collected air at N. T. P. in dry state.

$$\text{Then, } \frac{v_0 \times 760}{273} = \frac{v \times (P - f)}{273 + t} \quad \text{or} \quad v_0 = \frac{v(P - f)273}{(273 + t)760}$$

$$\text{Hence vapour density, } \rho_0 = \frac{g}{v_0} = \frac{g(273 + t)760}{v(P - f)273} \text{ gm/c.c.}$$

Problem : 0.16 gm of a substance gave by Victor Meyer's method 26.2 c.c. of displaced moist air measured at 17°C and 764 mm (aqueous tension at $17^\circ\text{C} = 14$ mm). Calculate the mol. wt. of the substance.

Let V = volume of the displaced air at N. T. P.

$$PV = \frac{g}{M} RT$$

$$\therefore \frac{(764 - 14)}{760} \times \frac{26.2}{1000} = \frac{0.16}{M} \times 0.082 \times (273 + 17)$$

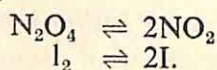
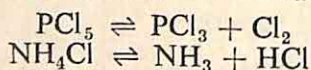
$$\text{or } M = 147.1$$

Problem : 0.2704 gm of a liquid was used in determining its mol. wt. by Hofmann's method. The volume of the vapour was 113 c.c. at 100°C. The atmospheric pressure was 747 mm and the height of mercury in the tube was 285 mm. What is the mol. wt.?

$$PV = \frac{g}{M} \cdot RT \quad \text{or} \quad M = \frac{gRT}{PV}$$

$$\therefore M = \frac{0.2704 \times 0.082 \times 373}{\frac{747-285}{760} \times 0.113} = 120.2$$

I.35. Abnormal Vapour Density : Gaseous Dissociation. For certain substances like ammonium chloride, phosphorous pentachloride, nitrogen peroxide, etc. the vapour densities are found to be less than expected. The measured densities decrease towards a limit as the temperature is raised. This is due to the splitting of the molecules into simpler ones at higher temperatures. With rise in temperature, the molecules in certain substances break up into simpler molecules and these simpler ones reunite to form the original molecules on cooling. This reversible phenomenon is called thermal dissociation. Examples :



In most cases, the limiting value of the vapour density at high temperatures is almost half of the theoretically calculated chemical value. For example, in nitrogen peroxide, as the temperature rises, more and more molecules dissociate and the total number of molecules in the gas increases. When practically all the molecules suffer dissociation, there will be twice the number of gm-molecules in the gas and the volume therefore will be double (Avogadro). The total weight remaining constant, the density will be about one-half of what is anticipated assuming no splitting up of the molecules. The dissociation thus explains the lowering of the vapour density with temperature-rise.

The occurrence of the thermal dissociation has been proved by the ingenious experiment devised by Than and Pebal. Some NH_4Cl is enclosed in a tube by the side of a porous partition made of compressed solid NH_4Cl . The tube is heated near the heap of NH_4Cl and a slow current of N_2 -gas is maintained in the tube on both sides of the partition (Fig. I.47). The vapours coming out with the N_2 -gas from the two ends are separately led into litmus solution. The gas escaping from the side of the solid NH_4Cl is found to be acidic while at the other end it is alkaline. This is due to the fact that NH_4Cl on dissociation gives equal proportion of NH_3 and HCl . Ammonia being lighter diffuses through the porous wall more readily

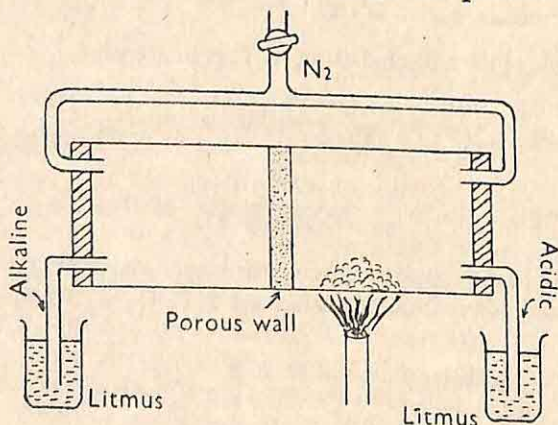


Fig. I.47. Experiment of Than and Pebal

than HCl -gas. So the gas coming out from the other side is alkaline due to excess of ammonia ; the gas coming out from the side of NH_4Cl is acidic due to excess of HCl . It therefore conclusively demonstrates the dissociation of ammonium chloride.

The extent of dissociation, *i.e.*, the fraction of the total number of molecules which suffers dissociation is called the *degree of dissociation*. Vapour density measurements can be used to determine the degree of dissociation. Let us take a general case where one molecule of a substance *A* splits up into *n* molecules of *B* on heating; *i.e.*, $A \rightleftharpoons nB$.

If *a* denotes the degree of dissociation, then at equilibrium at the higher temperature, for each gm-mole of *A*, there will be $(1-a)$ gm-moles of undissociated *A* and na gm-moles of *B*. So the total number of gm-moles of gas present would be $(1-a) + na$ or $1 + (n-1)a$.

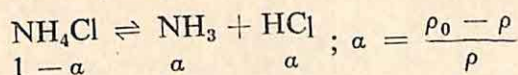
Let *V* be the volume occupied by 1 gm-mole of any gas at the pressure and temperature of the experiment. Now, if ρ_0 denotes the vapour density assuming absence of any dissociation, and if ρ denotes the observed vapour density when actual dissociation has occurred, we have for the total weight of the gas *W*,

$$W = \rho_0 V \quad \text{and} \quad W = \rho \cdot V [1 + (n-1)a]$$

$$\text{i.e.,} \quad \frac{\rho_0}{\rho} = 1 + (n-1)a \quad \text{or} \quad a = \frac{\rho_0 - \rho}{(n-1)\rho} \quad \dots (1.70)$$

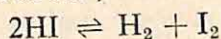
This relation is used to calculate the degree of dissociation. It is however implicit in this deduction that the pressure remains constant. We shall, later on, see that the degree of dissociation is not only influenced by temperature but by pressure also.

In equation (1.70), it may be remembered that *n* denotes the number of product molecules derived from each molecule of the original substance. The value of *n* is very often 2. Thus, for ammonium chloride dissociation, ($n = 2$)



The theoretically anticipated density ρ_0 is half the molecular weight and is calculated from the chemical formula. The degree of dissociation of many substances like COCl_2 , COBr_2 , CO_2 , SbCl_3 , SO_2Cl_2 , etc. has been studied from vapour density measurements.

It is necessary to point out here that in those cases, where there is no change in the number of molecules due to dissociation, there will be no net increase in volume and hence dissociation will not be accompanied with decrease in vapour density, *e.g.*, the dissociation of HI ;

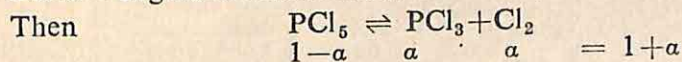


The vapour density is lowered only when the number of product molecules is greater than the number of molecules dissociating.

Some substances, like acetic acid, remain associated in the vapour phase. The extent of association may be ascertained by a similar method from vapour density determination.

Problem : 4.5 gm of PCl_5 on vaporization occupied a volume of 1700 c.c. at 1 atmosphere and 227°C . Calculate its degree of dissociation. ($P = 31$)

Let *a* = degree of dissociation. $M = 31 + 5 \times 35.5 = 208.5$



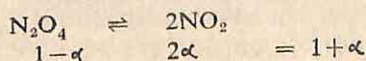
Or, each gm-mole changes into $(1+a)$ gm-moles.

$$\text{Hence,} \quad P_v = n(1+a)RT$$

$$\text{or} \quad 1 \times \frac{1700}{1000} = \frac{4.5}{208.5} (1+a) \times 0.082 \times (273+227)$$

$$\text{or} \quad a = 0.921 \text{ i.e., percentage of dissociation} = 92.1\%$$

Problem : At 60°C , the vapour density of nitrogen peroxide is 30.2. Calculate the percentage of NO_2 molecules by weight and by volume.



(i) The theoretical density of N_2O_4 : $\rho_0 = \frac{M}{2} = 46$

The observed density $\rho = \frac{\rho_0}{1+(n-1)a} = \frac{\rho_0}{1+a}$

or $a = \frac{\rho_0 - \rho}{\rho} = \frac{46 - 30.2}{30.2} = 0.523$

That is, the fraction of gm-moles decomposed = 0.523. Or, percentage of NO_2 moles by weight = 52.3%

(ii) In the mixture, the ratio of gm-moles of N_2O_4 and NO_2 is

$$\text{NO}_2 : \text{N}_2\text{O}_4 = \frac{2a}{1+a} : \frac{1-a}{1+a}$$

In accordance with Avogadro's Law, this is also the ratio of their volumes. Hence,

$$\text{Percentage of } \text{N}_2\text{O}_4 \text{ by volume} = \frac{1-0.523}{1+0.523} \times 100 = 31.3\%$$

$$\text{Percentage of } \text{NO}_2 \text{ by volume} = \frac{2 \times 0.523}{1+0.523} \times 100 = 68.7\%$$

COLLISION NUMBER : MEAN FREE PATH

I.36 Molecular Collisions. Owing to their incessant random motion at high speed the molecules experience an enormously large number of mutual impacts every second. The number of collisions an individual molecule suffers per second may be calculated in the following way.

Suppose in a gas there are n molecules present per c.c. Let σ be the diameter of each molecule. A given molecule 'A' will collide with the molecule 'B' when the distance between their centres is σ . Imagine, therefore, a sphere of radius σ around the centre of A. Any other molecule, whose centre would come within this sphere, will obviously collide with the given molecule 'A'. Now the molecule 'A' is moving with an average velocity c . The volume of colliding space that would be swept out by it in unit time will be $\pi\sigma^2c$ (Fig. I.48). Imagine further that all the other molecules are stationary. Then, the number of collisions which this molecule will suffer in 1 sec. is the number of molecules present in the volume $\pi\sigma^2c$ i.e., total number of collisions suffered by the molecule per second = $\pi\sigma^2cn$.

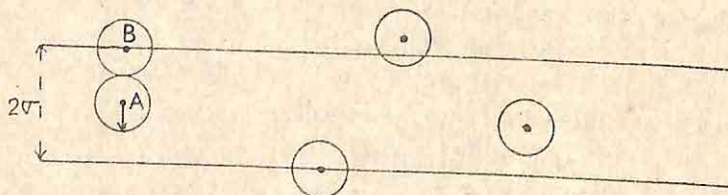


Fig. I.48 Molecular Collisions

For more accurate estimation of the collision number for a molecule we must remember that other molecules are not stationary and those are also in motion. It is therefore necessary to consider the relative velocity of the molecules. Two molecules may come on a head-on collision or a grazing collision or a collision at any angle. As all angles of collision are possible from 0° to 180° the average may

be taken as a 90° collision. The relative velocity will then be $\sqrt{2}c$ if c be the average velocity of a molecule as shown in Fig. I.49.

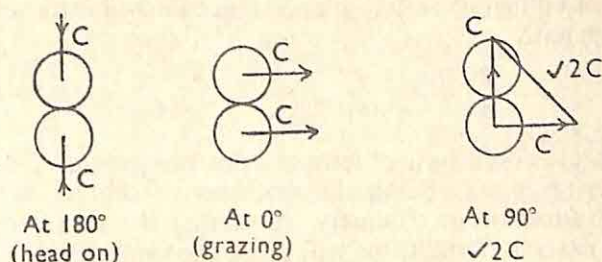


Fig. I.49

We can thus say, that,

the number of collisions suffered by a molecule per second

$$Z_1 = \sqrt{2}\pi\sigma^2cn \quad \dots (I.71)$$

The total number of collisions occurring per second in one c.c. of the gas,

$$Z = \frac{1}{2} n \cdot \sqrt{2}\pi\sigma^2cn = \frac{\pi\sigma^2cn^2}{\sqrt{2}} \quad \dots (I.72)$$

[The average velocity $c = \sqrt{8RT/\pi M}$]

The factor $\frac{1}{2}$ is necessary as each collision involves two molecules. Otherwise each collision would be counted twice.

If it is a mixture of two gases, then the number of collisions per c.c. per second is given by the expression,

$$Z_{AB} = (\sigma_a + \sigma_b)^2 \cdot \left(\frac{\pi RT}{2\mu} \right)^{\frac{1}{2}} \cdot n_a \cdot n_b \quad \dots (I.73)$$

where σ -terms are the diameters, and n -terms are the number of molecules per c.c. of the two species a and b of the mixture, and μ is the reduced mass. This expression can be derived easily from eqn. (I.72.) Let us first assume that both A and B molecules have the same diameter σ and mol. wt. M . There are n_a molecules of A and n_b molecules of B per c.c., i.e., total number of molecules per c.c. = $(n_a + n_b)$.

$\therefore$ From eqn. I.72,

$$\text{total number of collisions per c.c., } Z = \frac{1}{\sqrt{2}} \pi\sigma^2c \cdot (n_a + n_b)^2$$

Subtraction of the number of collisions involving just A molecules or just B molecules from this will give the number of collisions between A and B molecules. Hence,

$$\begin{aligned} Z_{AB} &= \frac{1}{\sqrt{2}} \pi\sigma^2c (n_a + n_b)^2 - \frac{1}{\sqrt{2}} \pi\sigma^2cn_a^2 - \frac{1}{\sqrt{2}} \pi\sigma^2cn_b^2 \\ &= \sqrt{2}\pi\sigma^2c \cdot n_a \cdot n_b. \end{aligned}$$

Now let us recognise the different diameters and molecular weights of molecules of A and B , so that mean diameter $\sigma = \frac{\sigma_a + \sigma_b}{2}$ and reduced mass $\mu = \frac{M_a \cdot M_b}{M_a + M_b}$;

$$\text{average velocity } c = \sqrt{\frac{8RT}{2\pi\mu}}.$$

Substituting these,

$$\begin{aligned} Z_{AB} &= \sqrt{2}\pi \left(\frac{\sigma_a + \sigma_b}{2} \right)^2 \cdot \sqrt{\frac{8RT}{2\pi\mu}} \cdot n_a \cdot n_b \\ &= (\sigma_a + \sigma_b)^2 \cdot \sqrt{\frac{\pi RT}{2\mu}} \cdot n_a \cdot n_b \quad \dots (I.73) \end{aligned}$$

1.37. Mean Free Path. The average distance travelled by a molecule between two successive collisions is known as the *mean free path* and is denoted by l . Since Z , is the number of collisions suffered by a molecule and c its velocity per second, then the mean free path

$$l = \frac{c}{Z} = \frac{c}{\sqrt{2}\pi\sigma^2cn} = \frac{1}{\sqrt{2}\pi\sigma^2n} \quad \dots (I.74)$$

Since under same conditions of temperature and pressure, n will be the same for different gases (Avogadro) and the diameter of molecules of different gases is generally of the same order, (namely, 10^{-8} cms) the mean free path of various gases under same external conditions will be of the same order.

At N. T. P. one mole of a gas occupies 22.4 litres, and Avogadro number is 6.02×10^{23} , so that $n = 2.7 \times 10^{19}$. Taking the diameter of a molecule as 2×10^{-8} cms, we have

$$l = \frac{1}{\sqrt{2}\pi(2 \times 10^{-8})^2 \times 2.7 \times 10^{19}} = 2.1 \times 10^{-5} \text{ cms}$$

i.e., under ordinary conditions, the mean free path is extremely small.

The equation (I.74) can be used to determine the mean free path only when the molecular diameter is known. A knowledge of viscosity of the gas also enables us to determine l , the mean free path, which we shall discuss presently.

1.38. Viscosity. The property of viscosity is associated with fluid flow. By viscosity is understood the internal friction between layers of fluid as they pass over each other when moving with different velocities. This property is exhibited by gases as well as liquid. It would be easier to understand this first with a flowing liquid. When a liquid is flowing steadily over a fixed horizontal surface, (i.e., the flow is stream-line), its layer in immediate contact with the fixed surface is stationary and the velocity of layers increases with the distance from the fixed surface (Fig. I.50).

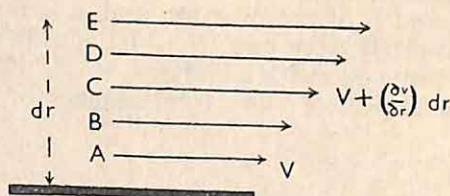


Fig. I.50

Considering any layer, the layer immediately beneath will try to retard it while the layer above will accelerate it. Thus there is a tendency to destroy the relative motion as if there is a tangential force dragging backwards. This is the viscous force. Newton showed that this force of internal friction ' f ' is directly proportional to the area of contact ' A ' and the velocity gradient $\frac{dv}{dr}$.

Hence,

$$f = -\eta A \frac{dv}{dr} \quad \dots (I.75)$$

The negative sign is indicative of the fact that the force is opposite to the direction of flow. It should be remembered that this motion is quite different from the diffusion flow and the internal frictional force is also quite different from the molecular attraction that we discussed earlier. The relation (I.75) is true for both gases and liquids, and is applicable only when the flow is laminar and steady and not turbulent and disorderly.

The proportionality constant η is called the *coefficient of viscosity*.

When $A = 1$ and $\frac{dv}{dr} = 1$, $\eta = -f$.

Hence we can define the coefficient of viscosity as the tangential force required

per unit area to maintain a unit velocity gradient, *i.e.*, to maintain unit difference of velocity between two layers unit distance apart. The coefficient of viscosity is expressed in units of *poise*, which in *cgs* system is dynes per sq. cm.

The flow of a fluid through a tube has been extensively studied in connection with viscosity. Consider a liquid (regarded as an incompressible fluid) flowing through a tube of uniform radius r and length L . The liquid layer at the walls of the tube is stagnant and the rate of flow of different layers increases as the centre is approached. The velocity is maximum at the centre of the tube (Fig. I.51). Let v be the velocity at a distance z from the centre, then from equation (I.75),

$$f = -\eta 2\pi z L \frac{dv}{dz}$$

For steady rate of flow, this force is exactly equal to the driving force $\pi z^2(P_1 - P_2)$ where P_1 and P_2 are pressures at the two ends. That is,

$$-\eta 2\pi z L \frac{dv}{dz} = \pi z^2(P_1 - P_2)$$

$$\text{or} \quad dv = -\frac{z}{2\eta L} (P_1 - P_2) dz$$

$$\text{or} \quad v = \frac{-(P_1 - P_2)}{4\eta L} z^2 + c \text{ (constant)}$$

When $v = 0$, $z = r$, under such conditions, we have

$$v = \frac{P_1 - P_2}{4\eta L} (r^2 - z^2)$$

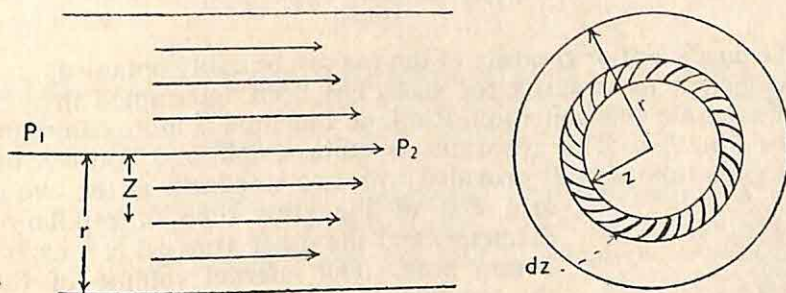


Fig. I.51

The total volume of liquid flowing through the tube per unit time is given by,

$$\frac{dV}{dt} = \int_0^r 2\pi z v dz = \int_0^r 2\pi z \frac{P_1 - P_2}{4\eta L} (r^2 - z^2) dz = \frac{\pi(P_1 - P_2)}{8\eta L} r^4$$

$$\text{or} \quad \eta = \frac{\pi(P_1 - P_2)r^4}{8L \left(\frac{\partial V}{\partial t} \right)} \quad \dots (I.76)$$

This is known as the Poiseuille's formula. It must be remembered that this relation is valid for incompressible fluid only.

I.39. Viscosity of Gases. Apparently, the relation (I.76) should also be applicable to the flow of gases through a tube. But gases are compressible and as such modification of the equation is necessary. The volume of a liquid (as well as the mass) flowing through any section of the tube per second can be regarded as constant, liquids being incompressible. But in the flow of gases through the tube,

the volume passing any sections of the tube per second is not constant, but the mass is constant. So, if V denotes the volume of a gas flowing across a section per second at a distance x from the entrance-point of the tube and ρ its density under pressure P over that section, we have

$$\rho V = \text{constant}$$

Since $\rho \propto P$, hence $PV = \text{constant}$.

If we consider a small section dx at a distance x from the entrance-point of the tube with a pressure difference dP across it, then by Poiseuille formula,

$$V = - \frac{\pi r^4}{8\eta} \frac{dP}{dx}$$

or multiplying both sides by P , we have

$$PV = - \frac{\pi r^4}{8\eta} P \frac{dP}{dx}$$

Now, if P_1 be the pressure at which the gas enters the tube and V_1 is the volume of the gas, then,

$$P_1 V_1 = PV$$

or $P_1 V_1 = - \frac{\pi r^4}{8\eta} P \frac{dP}{dx}$

or $\int_0^L P_1 V_1 dx = - \frac{\pi r^4}{8\eta} \int_{P_1}^{P_2} P dP$

where L is the length of the tube and P_1, P_2 are its end-pressures.

$$\therefore P_1 V_1 = \frac{\pi r^4}{16\eta L} (P_1^2 - P_2^2)$$

whence η the coefficient of viscosity of the gas can be easily obtained.

The coefficient of viscosity for gases has been determined in several ways. For a fairly accurate determination, Rankine's method is more commonly used.

Rankine's method. The apparatus is quite simple and consists of a closed rectangular glass tube $ABCD$ provided with two stopcocks at the two ends. One arm CD of the glass tube is capillary (0.2 mm diameter) and the other arm AB is a narrow tube of 3 mm bore. The internal volume of the tube V , the length l and the radius r of the capillary, the uniform cross-section a of the tube (AB), are all predetermined. A small pellet of mercury (length 3-4 cms) is introduced into the arm AB and is such that it can slowly move down under its own weight from fixed mark A to B . To begin with, the tube is filled with the gas and is kept vertically (in a constant temperature bath) with the mercury pellet in position A . The time required by the mercury pellet to move from A to B is noted. The quantity of gas forced through the capillary per second as the pellet moves down is thus known. From a knowledge of the weight of the mercury pellet (w) and the internal dimensions of the tube, the pressure difference under which the gas is flowing is also known. The volumes of gases v_1 and v_2 above and below the mercury pellet are also known. Applying the relation (I.76), it can be shown that

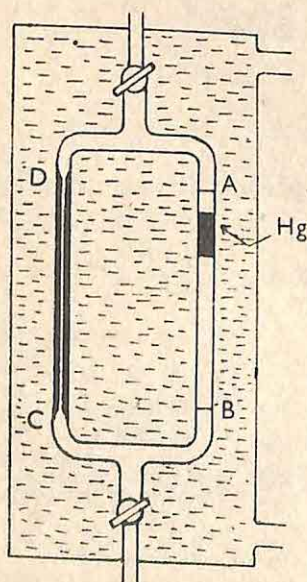


Fig. I.52 Rankine's apparatus

$$\eta = \frac{w\pi r^4 t}{8al(v_2 - v_1)}$$

where t is the time required by the pellet to move from A to B . The coefficient of viscosity of the gas is thus known.

I.40. Viscosity of Gases and Mean Free Path.

An explanation of the viscous drag in the gas-layer may be obtained from the kinetic theory. Consider a gas flowing in layers parallel to the XY -plane in the X -direction such that the layer adjacent to the XY -plane has a velocity $v = 0$ (Fig. I.53). As the distance of the layers along Z -axis increases, the velocity of the layers will also increase. Now if a molecule passes from A in the lower layer to B in the upper layer, it will carry to the latter a momentum less than the average momentum possessed by the molecules at the upper layer, for the velocity of the molecules in the lower layer is less than that of the molecules in the upper one. On the other hand, if a molecule passes from the upper to the lower layer, the latter will obtain a momentum higher than the average momentum possessed by molecules of the lower A -layer.

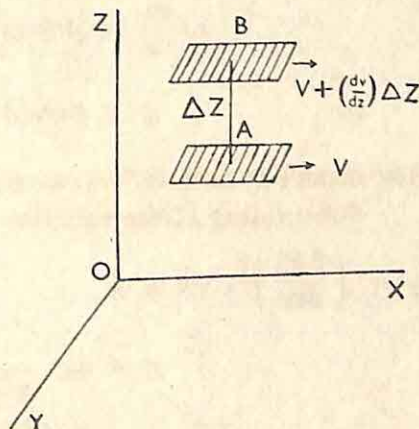


Fig. I.53

Now, apart from the laminar flow of the gas due to an external pressure, the molecules are all in random thermal motion. In consequence, there must occur interchange of molecules between the layers. The result is that the average velocities of the molecules of the upper layer will decrease and those of the lower layer will increase. This transport of momentum counteracts the relative velocities of the flowing gas layer. In other words, the transport of momentum is responsible for the viscous force.

Imagine a gas flowing in a horizontal direction (along OX direction in Fig I.53) such that the velocity of flow of the layer OX is zero and the velocity gradient along z -axis is (dv/dz) . Suppose the layer A has a velocity v .

If l be the mean free path of the molecules then the molecules which will reach the given level A from below will have a velocity, $v - l(dv/dz)$ and those molecules which will arrive from above will have a velocity, $v + l(dv/dz)$.

All directions being equally probable, on an average, one third of the molecules would be moving up and down along z -axis, of which one-half would go upwards and one-half downwards. If we consider a cross-section ' s ' of the gas layers, the number of molecules moving downwards will be $\frac{1}{6}nc_as$ per sec., where c_a is the average velocity of the molecules and ' n ' is the number of molecules per c.c. The momentum transported to the layer A per sec. from above is then $\frac{1}{6}mnc_as [v + l(\partial v/\partial z)]$, m being the mass of a molecule.

Similarly, considering molecules reaching A from below, the momentum transported from the opposite direction is $\frac{1}{6}mnc_as [v - l(\partial v/\partial z)]$.

The net transport of momentum to this layer per second is the difference of these two quantities.

$$\begin{aligned} &= \frac{1}{6}mnc_as [v + l(\partial v/\partial z)] - \frac{1}{6}mnc_as [v - l(\partial v/\partial z)] \\ &= \frac{1}{3}mnc_as l(\partial v/\partial z). \end{aligned}$$

This momentum-change per second is the force of internal friction.

$$\therefore \eta s \cdot \frac{dv}{dz} = \frac{1}{3} mn c_a s l \frac{dv}{dz},$$

$$\text{or} \quad \eta = \frac{1}{3} mn c_a l = \frac{1}{3} \rho c_a l \quad \dots (I.77)$$

The mean free path is thus calculated from the viscosity.

Substituting l from equation (I.74) and remembering average velocity

$$c_a = \left(\frac{8RT}{M\pi} \right)^{\frac{1}{2}}, \text{ we have}$$

$$\eta = \frac{1}{3} \rho \cdot \frac{1}{\sqrt{2\pi\sigma^2 n}} \left(\frac{8RT}{\pi M} \right)^{\frac{1}{2}}$$

$$\text{or} \quad \eta = \frac{2\sqrt{RTM}}{3(\pi)^{\frac{1}{2}} N_0 \sigma^2} \quad \dots (I.78)$$

It is evident that a knowledge of Avogadro's number (N_0) and the determination of viscosity enables us to find out the molecular dimensions (σ). Further we know that the van der Waals constant ' b ' is four times the actual volume of the molecules, i.e.,

$$b = 4 \times \frac{4}{3} \pi r^3 \times N_0 = \frac{2}{3} \pi N_0 \sigma^3 \quad \dots (I.79)$$

Multiplying (I.78) and (I.79) and re-arranging,

$$\sigma = \frac{2}{3} \eta b \sqrt{\frac{\pi}{RTM}} \quad \dots (I.80)$$

The van der Waals constant will thus give us the magnitude of the molecular diameter.

Problem : At N. T. P., the viscosity of hydrogen is 8.4×10^{-5} poise and the average velocity of the molecules is 1.7×10^5 cms/sec. Calculate the mean free path and the molecular diameter.

$$\text{Now,} \quad l = \frac{3\eta}{c_p} = \frac{3 \times 8.4 \times 10^{-5}}{1.7 \times 10^5 \times 9 \times 10^{-8}} = 1.6 \times 10^{-5} \text{ cms.}$$

From eqn. (I.74),

$$\sigma = \left(\frac{1}{\sqrt{2\pi n l}} \right)^{\frac{1}{2}} = \left(\frac{1}{\sqrt{2 \times 3.14 \times \frac{6 \times 10^{23}}{22400} \times 1.6 \times 10^{-5}}} \right)^{\frac{1}{2}}$$

$$= 2.24 \times 10^{-8} \text{ cms.}$$

Problem : Calculate the molecular diameter of oxygen. Given $\eta = 1.92 \times 10^{-4}$ at 0°C , $b = 31.2$ c.c.

$$\text{Since } \sigma = \frac{2}{3} \eta b \sqrt{\frac{\pi}{RTM}}, \text{ we have}$$

$$\sigma = \frac{2}{3} \times 1.92 \times 10^{-4} \times 31.2 \times \sqrt{\frac{3.14}{8.4 \times 10^7 \times 273 \times 32}}$$

$$= 2.7 \times 10^{-8} \text{ cms.} = 2.7 \text{ \AA}$$

The equation (I.78) shows that the coefficient of viscosity η is independent of pressure. This has actually been realised in practice specially at relatively low pressures. It is considered as a very strong argument in favour of the kinetic theory.

This equation further suggests that the coefficient of viscosity will be proportional to the square root of the absolute temperature. Experimentally however it

is found that the increase in viscosity coefficient is higher than that predicted by this relation. This deviation is due to the existence of the intermolecular attraction of the molecules which was not accounted for in applying the kinetic theory. A satisfactory empirical relation between the temperature and the viscosity coefficient has been suggested by Sutherland in the form ;

$$\eta = k_1 \frac{\sqrt{T}}{1 + \frac{T}{C}} \quad \dots (I.81)$$

where k_1 and C are constants for the gas. C is often called the Sutherland constant.

We may also consider here the influence of temperature and pressure on the mean free path, l , of the gas. We have

$$l = \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

At constant pressure, the number of molecules present per c.c. of the gas is inversely proportional to the absolute temperature (T). That is, l is directly proportional to the absolute temperature. Again, at constant temperature, n is directly proportional to the pressure and hence l is inversely proportional to the pressure.

I.41. Thermal Conductivity of Gases. In the previous section, it was seen that the viscosity is a consequence of the transport of momentum across a velocity-gradient. A similar transport phenomenon arises in the thermal conductivity of gases. The thermal conductivity of a gas is due to the transport of kinetic energy across a temperature gradient, *i.e.*, kinetic energy gradient.

The kinetic energy gradient is $\frac{dE}{dz}$ along Z -axis. Then, as in the case of viscosity, we may say, the net transport of energy per unit time across area s ,

$$\begin{aligned} &= \frac{1}{3} \bar{n} \bar{c} s \times l \frac{dE}{dz} \\ &= \frac{1}{3} \bar{n} \bar{c} s \times l \frac{dE}{dT} \cdot \frac{dT}{dz} \end{aligned}$$

where E = average kinetic energy per molecule. The amount of heat-flow per unit time is given by

$$Q = \kappa.s. \frac{dT}{dz}$$

where κ = the coefficient of thermal conductivity, *i.e.*, heat-flow per unit time per unit area across unit temperature gradient.

$$\text{Equating,} \quad \kappa.s. \frac{dT}{dz} = \frac{1}{3} \bar{n} \bar{c} s \frac{dE}{dT} \cdot \frac{dT}{dz}$$

$$\begin{aligned} \text{or} \quad \kappa &= \frac{1}{3} \bar{n} \bar{c} l \frac{dE}{dT} \\ &= \frac{1}{3} \bar{n} \bar{c} l m c_v = \frac{1}{3} \bar{\rho} \bar{c} l c_v \quad \dots (I.82) \end{aligned}$$

for, $dE = m c_v dT$, where c_v = heat-capacity per gm, and m = molecular mass. Comparing with the equation (I.78), we have

$$\kappa = \eta c_v \quad \dots (I.83)$$

Likewise, the diffusion in a gas is really the transport of mass across a concen-

tration gradient and in the same way it can be shown that the diffusion coefficient D is given by

$$D = \frac{1}{3} \bar{c} l \quad \dots (I.84)$$

or

$$D = \frac{\eta}{\rho} \quad \dots (I.85)$$

REFERENCES FOR FURTHER READING

- (1) Kinetic theory of Gases—Loeb
 - (2) Kinetic theory of Gases—Kennard
 - (3) Introduction to the Kinetic theory of gases—Jeans
 - (4) Treatise on physical chemistry—Vol. II, Taylor & Glasstone
 - (5) Treatise on Heat & Thermodynamics—Saha and Srivastava
- Also read : Roseman & Katzoff, *J. Chem. Edn* 11, 350, (1934) ; Swinbourne, *ibid*, 32, 366, (1955).

Problems

1. A gram of He gas is confined in a 2-litre flask under a pressure of 2.05 atmospheres. What is its temperature?
2. What is the density of CO_2 at 127°C if confined under a pressure of 2280 mm?
3. Find the total pressure exerted by 1.6 gms of methane and 2.2 gms of CO_2 contained in a 4 litre flask at 27°C .
4. At 27°C , half-a-litre of hydrogen measured at 500 mm of mercury, and a litre of oxygen measured at 400 mm of mercury are introduced into an evacuated 1-litre vessel. Calculate the resulting pressure.
5. The rate of diffusion of a volatile metallic flouride containing 32.39% fluorine is 13.27 times as slow as that of hydrogen. Establish the formula of the flouride and the atomic weight of the metal.
6. 100 c.c. of iodine vapour at 600°C took 125 sec. to effuse through a hole. An equal volume of oxygen under similar conditions required 50 seconds. Calculate degree of dissociation of iodine vapour at 600°C .
7. In a vessel of volume 0.62 litres at 1 atm. 2.2 gms of phosphorus pentachloride was completely vaporized at 200°C . Calculate the degree of dissociation of phosphorus pentachloride.
8. Calculate the mol. wt. of chloroform from the data obtained by Victor Meyer's method : 0.22 gms of chloroform displaced 45 c.c. of air measured at 20°C and 755 mm pressure. Aqueous tension at 20°C is 17.4 mm.
9. Calculate the root mean square velocities in centimeters per second for (i) CO_2 molecules at 27°C , (ii) Deuterium molecules at N. T. P.
10. Calculate r.m.s., average and most probable velocities in cms per second of O_2 at 0°C .
11. Find out the kinetic energy of translation in ergs of 5 moles of a perfect gas at 0°C .
12. What is the kinetic energy of 2 gm-moles of an ideal gas occupying a volume of 5 litres under a pressure of 10 atmospheres?
13. If the density of helium be 0.18 gms/litre at 760 mm, what is the molecular velocity?
14. Find out the number of molecules present per c.c. in a vessel evacuated to a pressure of 10^{-6} mm at 27°C .
15. Calculate the number of bimolecular collisions per c.c. in helium gas at N. T. P ; the diameter of helium atom is $2.18 \text{ \AA}$.
16. For carbon dioxide, $T_c = 300^\circ\text{K}$ and its critical density is 0.45 gms/c.c., calculate van der Waals constants.
17. Sulphur dioxide is a van der Waals gas. Three gm-moles of the gas occupy 10 litres at 15 atm. Find out its temperature.
18. Molar volume of helium at 100 atmospheres and 0°C is 0.01107 times the volume at 1 atmosphere and 0°C . Assess the radius of the helium atom. Assume the intermolecular attraction between He-atoms is negligible.

[Ans. $r = 1.34 \text{ \AA}$]

19. For argon, $T_c = -122^\circ\text{C}$ and $P_c = 48$ atmospheres. What is the radius of the argon atom?
20. At N. T. P. the viscosity of hydrogen is 8.4×10^{-5} poise. Its density is 9×10^{-5} gm/c.c. The velocity of H_2 -molecules is 1.7×10^5 cms/sec. Find out the diameter of the molecule.
21. Define electron-volt unit of energy. Calculate the number of ergs per molecule, and kilocalories per gm-mole corresponding to 1 electron-volt per molecule.
22. The diameter of argon is $2.86 \text{ \AA}$. What is the mean free path of argon at 25°C and 1 atmosphere pressure?
23. The sp. heat of a gas at constant volume is 0.075 and that at constant pressure is 0.125. What is the mol. wt. of the gas? [Ans : 40]
24. Write the integral which expresses the total amount of energy held by molecules with energies greater than some value, say ϵ_1 .
What fraction of molecules have energies greater than $10 kT$?
25. Compare the volume of 10 gms of HCl gas at 100°C and 25 atmosphere pressure given by ideal gas law with that given by van der Waals relation.
($a = 3.67 \text{ atm litres}^2/\text{mole}^2$; $b = 4 \times 10^{-2} \text{ litres/mole}$)
26. At 27°C , what will be the ratio of reduced temperatures of CO_2 and NH_3 ?
27. Show that the reduced form of the Berthelots equation of state would be

$$\pi \phi = \left[\frac{32}{9} \theta + \frac{\pi}{4\theta} \left(1 - \frac{6}{\theta^2} \right) \right]$$

28. Calculate the heat that will be given out when 2 moles of Argon are cooled from 100°C to 0°C at (i) constant volume and (ii) constant pressure.
29. At 27°C , the viscosity coefficient of a gas is 150 micropoise at 1 atm. Find the molecular diameter of the gas molecule.
(b) At 0°C , η for oxygen is 103×10^{-6} poise. What is its molecular diameter?
30. The limiting density of hydrogen bromide is 3.610 at 0°C . Calculate the exact at. wt. of bromine. [$H = 1.008$]

$$[\text{Note : } M = \lim_{p \rightarrow 0} (d/p)RT]$$

[Ans : 79.851]

31. 'In an experiment with HCl -gas, the following data were obtained,
normal density = 1.6391 gms/litre
 $P_1 V_1 = 5481$ $p_0 v_0 = 5521$

Given the limiting density of hydrogen as 0.089922, find out the true atomic weight of chlorine. [Ans : 35.466]

32. At 520°C , the vapour density of PCl_5 was found to be 57.92. What percentage of the pentachloride is dissociated? [Ans : 79.98%]

THE LIQUID STATE

II.1. The Liquid State. When a gas is gradually cooled, it changes into the liquid state by a process of condensation. On further cooling the liquid freezes into the solid state. On heating a solid the reverse changes are observed. The liquid state is thus an intermediate one between the gaseous and the solid states. This statement is however a qualitative one only. For, every property of the liquid is not necessarily intermediate in value between those of the other two states. In fact, a liquid has some of the properties of the solid and some of the properties of the gas. When the magnitudes of the different properties of the liquid are examined, it is generally found that some of the properties approach those of the solid while others are quite close to those of the gas.

In the solid state, due to strong cohesive forces the molecules are tied together in a regular pattern and free motion except oscillation is forbidden. In the gaseous state the molecules are in utmost chaotic motion due to very little cohesive forces and their potential energy is negligible. In a liquid we do not find the random motion as observed in gases, nor do we have the perfect orderliness of the crystals. In liquid state, the molecules have intermediate order of potential energies and cohesive forces.

Experiments show that there is a relatively small increase in volume (about 10 per cent) during the fusion of a solid. This means that at least near about the melting point the density or volume of the liquid does not appreciably alter from that of the solid state. Again, the latent heat of fusion is much less than the latent heat of vaporisation. The specific heats of a substance in the solid and the liquid state approach each other, specially in the neighbourhood of the freezing point (See Table below). These indicate that the nature of the motion in the liquid state and in the solid state are fundamentally the same. In other words, the arrangement of molecules in a liquid is more or less similar to their arrangement in the solid. The low latent heat of fusion suggests that the cohesive forces between the molecules decrease only to a small extent when the solid is transformed into the liquid. The existence of cohesion is also responsible for the fact that both solids and liquids maintain a free surface. The other resemblance between the solids and the liquids is their relative incompressibility compared to gases. The compressibilities of solids and liquids are of the order of 10^{-6} and 10^{-5} per atmosphere whereas the compressibility of a gas is the reciprocal of the pressure. On the other hand, the lack of rigidity is the most notable resemblance between the liquids and the gases. In consequence neither a liquid nor a gas can offer permanent resistance to a shearing stress and they, therefore, take the shape of the container. Near about the critical temperature and specially at high pressures, the behaviour of liquids approximates that of gases. This we have already observed in the study of Andrews curves (Fig. I.8).

Substance	Density		Latent heat		Specific heat	
	Solid	Liquid	Fusion	Vaporisation	Solid	Liquid
Na	0.97	0.93	630	23300	7.6	8.0
Hg	14.19	13.60	560	24200	6.7	6.7
Zn	7.14	6.92	1800	27700	7.2	7.9
Cl ₂	2.2	1.6	765	2439	14.0	16.2
CH ₄	—	—	—	1952	10.6	13.5
H ₂ O	0.915	1.00	1434.6	9712.8	8.82	18.14

The facts stated above enable us to obtain an approximate idea regarding the structure of liquids. The compactness and cohesion observed in the liquid are

indicative of a structure similar to that in a solid while the comparative ease with which the liquids flow or diffuse indicates a disordered random structure like that occurring in a gas. In a crystal we have a perfect and well ordered arrangement of the molecules throughout the entire mass ; each molecule is surrounded by a set of other molecules in a particular symmetrical pattern. Since on melting a crystal expands only about 10 per cent in volume or about 3 per cent in intermolecular spacing, it is only reasonable to conclude that a molecule in the liquid state must still remain in the vicinity of some molecules surrounding it. The molecular arrangement cannot be as random as in a gas and there cannot be a great deal of freedom of movement. The ordered arrangement is not therefore completely destroyed when the solid is liquefied. The crystal structure involves rigorous geometrical order. The thermal motions introduce a disorder. It is certain that the introduction of a small region of disorder into a crystal would cause disturbance in the long range and destroy the crystalline arrangement. That is why there

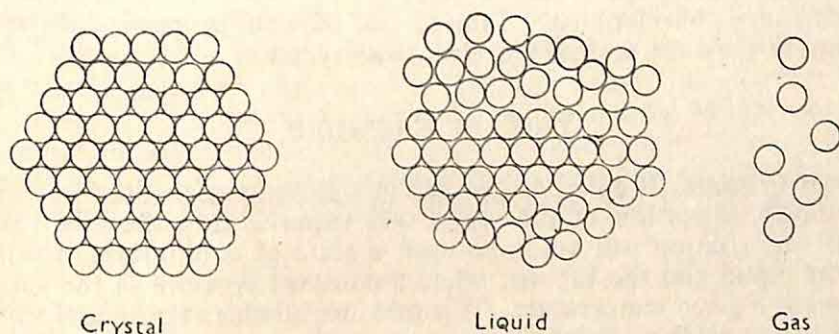


Fig. II.1

is an abrupt variation in the properties between solids and liquids. This explains the sharpness of the melting points. This idea has been clearly illustrated by J.D. Bernal's two dimensional models (Fig. II.1) of solid, liquid and gas. A small disorder is introduced into the liquid by permitting only five surrounding atoms to an atom instead of six atoms as provided in the solid. The remaining circles (atoms) were then drawn in the utmost possible ordered arrangement. The results show that the disorder must appear in long ranges in diverse directions though islets of small range order do remain. That is, when the thermal motion causes a disorder in one region, it spreads in all directions destroying the entire regular structure. The liquid may therefore be considered to have a structure like that of a crystal except that the well-ordered pattern extends over a short range instead of over the entire mass. This has been called "*short range order and long range disorder*." It must however be emphasised that the short range order in the liquid structure is continuously changing because of the thermal motion.

Stewart however suggested a somewhat different structure. According to him, there are in a liquid large numbers of well-ordered groups, each containing a few hundred molecules. These regularly ordered small groups are called 'cybotactic' groups. In between the cybotactic groups are embedded in a mass of disorganised molecules. In other words, the cybotactic groups are permanent and there is a dynamic equilibrium between the cybotactic groups and the disordered molecules. In any case, there exists short range order in the liquid.

The studies in X-ray diffraction of the liquids bear evidence in support of the short-range order. If the liquid were completely devoid of regularity of structure there would be a continuous scattering of X-rays without maxima or minima. But in actual experiment, a few maxima and minima, indicating the existence of regular pattern or order, are observed in the liquid. That the number of these maxima or minima is small, suggests the existence of the short-range order only.

To develop mathematically a theory for liquids like the one for gases is an extremely difficult task, particularly for the complex molecular configurations involved. Some attempts made recently met with considerable success. Eyring con-

siders the liquid to some extent similar to a gas. In a gas the molecules freely move about the entire space; the excluded volume which is physically occupied by the molecules is negligible. In the liquid, the position is the reverse, the space occupied by the liquid is mostly occupied by the molecules and a comparatively small space is void. The void space in which the centres of molecules execute motion is called the *free volume*. Eyring succeeded to correlate this free volume with many properties of the liquid. Another concept has been developed primarily based on the order-disorder idea. There are vacant positions in the ordered pattern and these are called 'holes'. It may be imagined that the free volume of Eyring is distributed in the form of holes. These holes may be of various sizes. The liquid may be conceived of mostly as a material substance with a few holes moving at random. With rise of temperature, the concentration of holes in the liquid also increases. A molecule has the probability of occupying a position in the ordered lattice or in a hole. The mathematical approach in either of these concepts is very complicated and is beyond the scope of this volume.

We may now consider some of the typical physical properties of the liquids, such as vapour-pressure, surface tension, viscosity, etc.

VAPOUR PRESSURE

II.2. Vapour Pressure. If a liquid is placed in a closed vessel with some free space over the liquid, a portion of the liquid will vaporise into the free space. The process of vaporisation will continue until a state of equilibrium is established between the liquid and the vapour, when a constant pressure of the vapour will be obtained at a given temperature. This pressure at which liquid and vapour can co-exist is the *saturation vapour pressure*, or simply, *vapour pressure* of the liquid at the given temperature. Thus, if a liquid is introduced into an evacuated vessel, the vaporisation would immediately start and continue until the saturation vapour pressure is reached. The vapour pressure is then a measure of the tendency for vaporisation of the liquid. As more and more molecules accumulate in the vapour phase, a tendency to condense back into the liquid phase also develops. At equilibrium, the rate of evaporation of the molecules of the liquid equals the rate of condensation of the vapour molecules into liquid. In other words, the equilibrium is a dynamic one; the processes are occurring in the opposite directions at equal speed. So long as the pressure of the vapour is less than the saturation pressure, the liquids will have a greater tendency to vaporise. The vapour pressure depends only on the temperature and is independent of the quantity of the liquid or the space occupied by the vapour. An idea of the physical change may also be conceived kinetically. The molecules in the liquid state are in continuous motion like the gas molecules, though the mean free path is much smaller. In consequence, the mutual attraction between the molecules is much larger. Within the bulk, the attraction on a molecule is more or less balanced from all directions but for a molecule on the surface, there would be much greater attraction inwards than that towards the free space. In order to pass into the vapour phase, the surface molecule must possess sufficient energy to overcome the force of attraction.

If E denotes the excess energy (per gm-mole) to be possessed in order to overcome the force of attraction and vaporise, then the number of molecules n_1 having energy more than E (per gm-mole) is given by eqn. (I.42a)

$$n_1 = n_l e^{-E/RT}$$

where n_l is the number of molecules per c.c. of the liquid.

If n_g denotes the number of molecules per c.c. of the vapour, the rate of condensation of the vapour molecules will be given by $\lambda' n_g$ where λ' is a constant. At equilibrium, the rates of condensation and evaporation would be equal and hence,

$$\lambda' n_g = n_l e^{-E/RT}$$

isoteniscope is kept in a thermostat and the outer limb of the U-tube is attached to a large bottle 'X' to stabilise the pressure. To the system is then attached a manometer *M* and a pressure regulator (pump *P* and air inlet *Q*). All connections are leak-proof. To make the determination, two-thirds of the bulb *A* and the U-tube are filled up with the liquid under investigation. The pressure is then reduced with the pump until the liquid in *A* boils and the air in the isoteniscope is displaced. The pressure is now slowly increased by admission of air through *Q*, until the liquid-levels in the U-tube are the same, sufficient time being allowed to attain a constant temperature. The manometer and the barometer readings are taken. The vapour pressure is the barometric pressure minus the pressure recorded in the manometer.

The method of Ramsay and Young is ingenious and gives results of a higher degree of accuracy. The experimental arrangement in outline is shown in Fig. II.3. A strong-walled boiling tube provided with a side-tube is used. Its mouth is closed by means of a rubber cork carrying a thermometer and a dropping funnel with a narrow bent stem. The bulb of the thermometer is kept covered with a thin cotton-wool wrap kept moist with the liquid to be studied. The tap-funnel supplies the liquid in small drops to keep the cotton-wool always moist. The boiling tube is kept immersed in a bath and the film of liquid in the cotton-wool evaporates by heat of radiation.

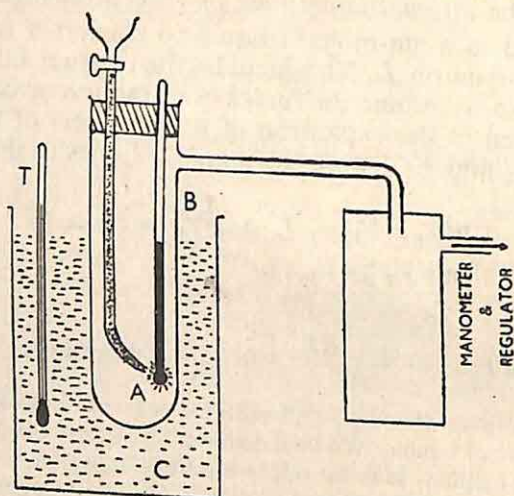


Fig. II.3. Ramsay & Young apparatus

The side-tube is attached to an empty bottle (for pressure stabilisation) and finally to a manometer and pressure regulator as in the previous experiment. In making a measurement, the pressure is first reduced, and the evaporation of liquid from the cotton-wool takes place. At a given pressure, a steady state is reached when the thermometer shows a constant reading and distillation from the surface of the thermometer bulb proceeds smoothly. The manometric reading indicates the vapour pressure at that temperature. By regulating the pressure, it is possible to measure vapour pressure at different temperatures.

Smith and Menzies developed another method, in which a bent narrow tube with a small bulb at one end is attached to a thermometer with a string. It is kept immersed in liquid paraffin kept in a boiling tube (Fig. II.4). The bulb contains the liquid to be studied. The boiling tube is connected to a pressure reservoir, manometer and pressure regulator as in the previous cases. The pressure is suitably reduced and the temperature of the paraffin bath adequately raised, when the liquid in the bulb boils and begins to escape as minute bubbles. The pressure is then cautiously raised by admitting air, until the bubbles just cease. The pressure and temperature are then recorded. To obtain the accurate pressure, corrections for the column of paraffin must also be made.

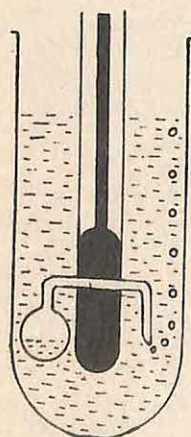


Fig. II.4

In the transpiration method, air or an inert gas in the form of fine bubbles is passed through the liquid maintained in a thermostat at temperature *T*. The gas is thus saturated with the vapour of the liquid. The volume *v* of the gas is determined and also the weight (*g*) of the liquid vaporised. The latter is obtained from the loss of the weight of the liquid.

Then,
$$p = \frac{g}{M_v} RT \quad (M = \text{mol. wt. of the vapour})$$

where p is the partial pressure of the vapour, i.e., the vapour-pressure. This method has been employed specially in determination of vapour pressures of several molten metals.

The vapour-pressures of some commonly used liquids are given in the Table below.

VAPOUR PRESSURES OF LIQUIDS IN MILLIMETERS

Temp. °C	H ₂ O	C ₂ H ₅ OH	C ₆ H ₆	C ₆ H ₅ CH ₃	CCl ₄	CHCl ₃	CH ₃ COOH
10	9.2	23.8	45.2	—	56.0	100.5	—
20	17.5	43.9	75.6	—	91.0	159.6	11.7
30	31.8	78.8	120.2	36.7	143.0	246.0	20.6
40	55.3	135.3	183.6	59.1	215.8	366.4	34.8
50	92.5	222.2	271.4	92.6	317.0	526.0	56.6
60	149.4	352.7	390.1	139.5	450.8	739.6	88.9
70	233.7	542.5	547.4	202.4	622.3	—	136.0
80	355.1	—	753.6	289.7	—	—	202.3
90	525.8	—	—	404.6	—	—	293.7
100	760.0	—	—	557.2	—	—	417.1

II.4. Vapour Pressure and External Pressure. So far it was presumed that the liquid was under the pressure of its own vapour only. But if the liquid is subjected to higher external pressures, then the vapour pressure changes. The relation between the vapour pressure and the external pressure is given by Gibbs equation in the form,

$$V_g dp = V_l dP$$

where V_g and V_l are the molar volumes of the vapour and the liquid at the given temperature T . The vapour pressure is given by p and external pressure by P . Assuming ideal gas laws, we have,

$$\frac{dp}{p} = \frac{V_l}{RT} dP$$

or

$$\ln \frac{p_1}{p_2} = \frac{V_l}{RT} (P_1 - P_2)$$

where p_1 and p_2 are the vapour pressures under external pressures P_1 and P_2 . The molar volume V_l is regarded as independent of pressure.

Problem : Calculate the increase in vapour-pressure of water per atmosphere-rise in external pressure at 10°C. (The v.p. of water at 10°C = 9.2 mm.)

$$\ln \frac{p_1}{p_2} = \frac{18(2-1)}{82.05 \times 283} \quad [\text{Since } V_l = 18 \text{ c.c., } R = 82.05 \text{ c.c. atm. per degree}]$$

$$\text{or } \log \frac{p_1}{p_2} = 0.0004, \quad \text{whence } p_1 = 1.001 p_2.$$

$$\text{or } \Delta p = p_1 - p_2 = 0.001 p_2$$

That is, the vapour-pressure increases by 0.1 % of its magnitude for one atmosphere rise in external pressure.

II.5. Internal Pressure. There are forces of attraction or cohesive forces between the molecules in a system. These forces depend on the intermolecular distances. In the case of gases, the forces are quite small because of the large intermolecular distances. But in the case of liquids, the cohesive forces are of primary importance. When the molecules are however in very close proximity, there also arise the repulsive forces of appreciable magnitude. The resultant of the forces of attraction and repulsion is called the *internal pressure*, P_t . Evidently the internal pressure will depend upon the volume of the liquid (V). Any increase in volume will involve

performance of work against the internal pressure. Now, if U denotes the inherent energy of the given mass of liquid, which is called internal energy in thermodynamic terms, then $\left(\frac{\partial U}{\partial V}\right) dV$ denotes the energy-change associated with the volume-change at constant temperature. This is equal to the work performed in expanding the liquid by volume dV against internal pressure P_i . That is,

$$P_i dV = \left(\frac{\partial U}{\partial V}\right)_T dV, \quad \text{or} \quad P_i = \left(\frac{\partial U}{\partial V}\right)_T \quad \dots (II.4)$$

It can be reasonably assumed that the internal latent heat of vaporisation is the work done in vaporisation of a gm-mole of liquid of volume V against the internal pressure P_i . Then,

$$L_i = \left(\frac{\partial U}{\partial V}\right)_T V = P_i V, \quad \text{or} \quad P_i = \frac{L_i}{V} \quad \dots (II.5)$$

from which the internal pressure P_i may be evaluated.

Again, anticipating a thermodynamic relation $\left(\frac{dU}{dV}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$, where P is the external pressure and $\left(\frac{\partial P}{\partial T}\right)_V$ is the pressure-coefficient, and assuming that van der Waals equation is also valid for liquids, we can write,

$$P_i = \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = \left(P + \frac{a}{V^2}\right) - P = \frac{a}{V^2} \quad \dots (II.6)$$

SURFACE TENSION

II.6. Surface Tension. Surface tension is the most significant of the characteristic properties of liquids. Consider a liquid in contact with its vapour. A molecule in the bulk of the liquid is subjected to forces of attraction from all directions by the surrounding molecules and is practically in a uniform field of force. But for a molecule at the surface, the net attraction towards the bulk of the liquid is much greater than that towards the vapour where the attracting molecules are more widely dispersed (Fig. II.5). This means that the molecules at the surface are pulled inwards. The result is liquid surfaces in absence of other forces tend to contract to minimum areas. The surface layer seems to behave as a stretched membrane and this pseudo-membrane tends to contract. It explains why a small amount of liquid, left freely, such as mercury, rain drop, etc., always takes spherical shape; because the sphere, for a given volume, has the least surface area.

That there is such a pull on the molecules of the surface layer can be easily demonstrated. If a circular copper-wire ring having a silk-thread tied loosely to the two opposite points be dipped into a soap solution so that on withdrawal a thin film stretches across the entire ring, the thread will freely swim in the film

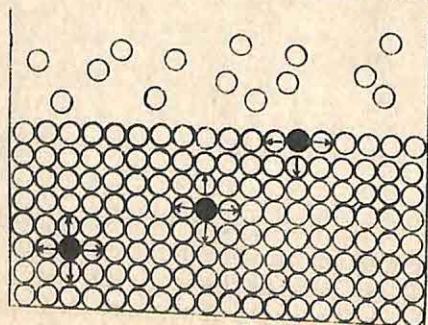


Fig. II.5

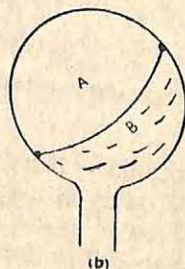
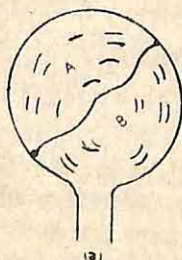


Fig. II.6

being attracted in all directions (Fig. II.6a). But if the film is punctured in one

part, say A , the thread will be pulled now in the direction of B only (Fig. II.6b) where the film is intact. The thread will immediately assume the most-stretched position.

The floating of metallic needles in water, the dancing of camphor on water, the rise of water-level in capillary tubes are all phenomena due to surface tension.

Now, since the surface is in a state of tension, an attempt to make a penetration along any line in the surface will require an application of force to hold the separate portions of the surface together. This force is called the *surface tension*, denoted usually by the symbol γ . It is expressed as the force in dynes per unit length acting at right angles to the line along the surface of the liquid.

Any increase in the area of the surface of a liquid against its natural tendency to contract will require performance of work. Consider a liquid film $PQRS$ contained in a rectangular wire-frame, in which the side PQ is movable (Fig. II.7). Suppose now the film is stretched by moving the boundary PQ by x cms to $P'Q'$. The length of PQ is l cms. If γ be the surface tension acting per cm, the force acting towards the film is $\gamma \cdot 2l$. It is to be remembered that there are two surfaces of the film.

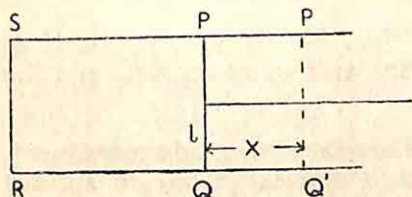


Fig. II.7

The work done in stretching the film,

$$W = \gamma \cdot 2l \times x = \gamma \cdot 2xl = \gamma \cdot \Delta A \quad \dots (II.7a)$$

or

$$\gamma = \frac{W}{\Delta A}$$

ΔA is the total area of the new surfaces created on the two sides of the film.

The work (in ergs) necessary to create or extend one sq. cm. of surface area is called the *surface energy* of the liquid per sq. cm. In other words, the surface tension is numerically the same as the surface energy of the liquid per unit area. The total surface energy is obtained by multiplying the surface tension of the liquid by its area.

II.7. Angle of Contact and Wetting of Surface. The surface of contact near its point of contact with a solid is generally a curved one. The angle between the tangent to the liquid surface at the point of contact and the solid surface, inside the liquid, is called the *angle of contact* for that pair of liquid and solid. The angle of contact, which depends upon the nature of the liquid and the solid, may obviously have values between 0° and 180° (Fig. II.8). For water and glass it is approximately 18° , whereas for mercury and glass it is nearly 140° .

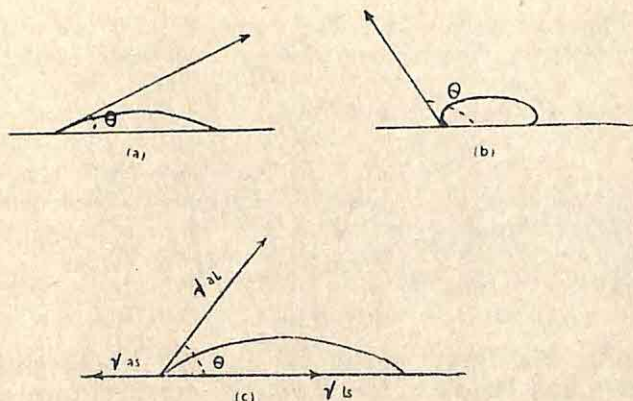


Fig. II.8

It is also common experience that some liquids spontaneously wet the surface of some solids and spread over them while other liquids do not wet and spread on certain surfaces. Thus water on glass, alcohol on glass or cement, oil on cloth

will easily wet the surface and spread over them but mercury on glass, water on solid paraffin, etc. will not wet or spread. This can be understood from the following consideration. In Fig. II.8 (c), let γ_{ls} , γ_{as} , γ_{al} denote the surface tensions for liquid-solid, air-solid and air-liquid respectively. The liquid on solidification does not lose its surface-tension, though the outward manifestations are not seen on account of the rigidity of the solid. When there is equilibrium,

$$\gamma_{as} = \gamma_{ls} + \gamma_{al} \cos \theta \quad \dots (II.7)$$

where θ is the angle of contact of the liquid with the solid.

If $\gamma_{as} > \gamma_{ls} + \gamma_{al} \cos \theta$, then there cannot be any equilibrium and the liquid will spread over the solid. From above, we have,

$$\cos \theta = \frac{\gamma_{as} - \gamma_{ls}}{\gamma_{al}}$$

If $\gamma_{as} > \gamma_{ls}$, then $\cos \theta$ is positive, i.e., θ is less than 90° . If $\gamma_{ls} > \gamma_{as}$, $\cos \theta$ is negative and θ is more than 90° . The first is the case with water on glass and the second with mercury on glass.

II.8. Pressure on a Curved Surface and Surface Tension. As already mentioned, very often the free surface of a liquid is curved. There exists due to surface tension an inward pressure. At equilibrium, this must be counter-balanced by a pressure acting outwards. Let $ABCD$ be a small portion of a cylindrical curved surface, i.e., curved in one direction only (Fig. II.9a). The surface tensions act on unit lengths and as such the forces along AB and CD cancel one another being

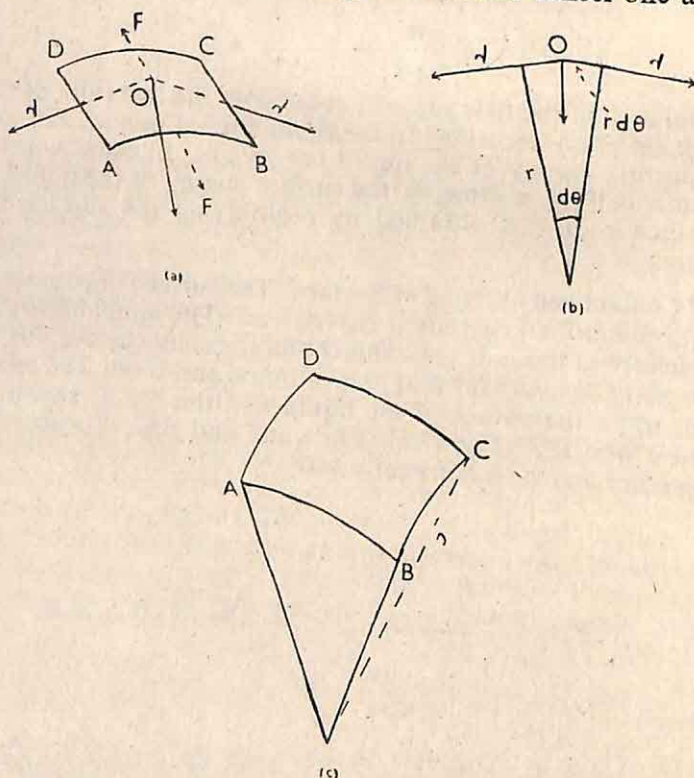


Fig. II.9

equal and opposite. The forces along AD and BC would give a resultant. In Fig. (b) consider a unit length in the direction AD . The force at each end is γ dynes. Assuming the curvature to be small, the resultant force meeting the surface at O is $\gamma d\theta$. The outward pressure P per unit area of this portion is $pr d\theta$, where r is the radius of curvature. At equilibrium,

$$pr d\theta = \gamma d\theta, \text{ or } p = \frac{\gamma}{r} \quad \dots (II.8)$$

This pressure p really counteracts the surface tension effect and will be directed outwards, for, the pressure on the concave side must be greater than on the convex side.

Further if we consider the surface also curved at right angles to the first direction, for which the radius of curvature is r' , then there would be another pressure due to this second curvature as in Fig. II.9a. The total resultant pressure due to the two curvatures at rt. angles, would be,

$$P = p + p' = \frac{\gamma}{r} + \frac{\gamma}{r'} = \gamma \left[\frac{1}{r} + \frac{1}{r'} \right]$$

If the surface is spherical, $r = r'$, so

$$P = \frac{2\gamma}{r} \quad \dots (II.9)$$

II.9. Rise of Liquid in a Capillary Tube. A very interesting effect of surface tension is the rise of liquid in a capillary tube. If a capillary tube is partly immersed vertically in a liquid, which wets the surface, the meniscus of liquid within the tube will be concave upwards, as in Fig. II.10(a). The result is that at the point A just below the surface in the tube, pressure will be less than that on the vapour

side above by an amount $\frac{2\gamma}{a}$ where a is the radius of

curvature of the meniscus. On the other hand, the pressure at the point B where the surface is flat, there is scarcely any difference of pressure on the two sides of the surface. But the pressure on the vapour side both in the tube and outside are the same. Hence inside the liquid the pressure at the point B will be higher than the pressure at the point A . The liquid therefore is pushed up the capillary tube until the level reaches the point C . The pressures at A and B are now equal because of the excess hydrostatic pressure over A . The equilibrium is thus attained, (Fig. II.10b). It can be easily understood that if the liquid does not wet the tube-surface, the meniscus would be convex upwards, and the liquid-level inside will be depressed.

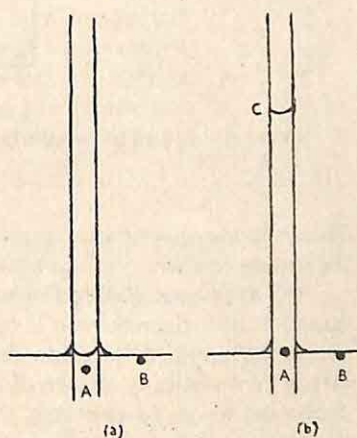


Fig. II.10

II.10. Measurement of Surface Tension. A variety of methods are employed for measuring surface tension. Only a few of these will be mentioned here.

(a) *Capillary Rise Method*: A thoroughly cleaned capillary glass tube of uniform bore is kept partly immersed in the experimental liquid in a vertical position. The liquid rises in the tube and attains a particular height. The height h of the liquid from the surface of the bulk outside to the bottom of the meniscus (Fig. II.11) is carefully measured with a travelling microscope. The radius r of the capillary tube is predetermined by the usual method of inserting a pellet of mercury and measuring its length and weight.

The upper meniscus is concave and if θ be the angle of contact then, the vertical component of the surface tension (γ) will be $\gamma \cos \theta$. The contact line of the meniscus with the wall of the tube is $2\pi r$. Hence the net upward pull is $2\pi r \gamma \cos \theta$. This is balanced by the weight of the liquid which has been drawn up. The weight of the liquid column is $(\pi r^2 h + v) \rho g$, where v is the volume of the liquid in the curved meniscus itself, and ρ is the density of the liquid. Then,

$$2\pi r \gamma \cos \theta = (\pi r^2 h + v) \rho g$$

The radius of curvature of the concave meniscus may be taken to be the same as the radius of the capillary tube.

So,

$$v = \pi r^3 - \frac{2}{3} \pi r^3 = \frac{1}{3} \pi r^3$$

Substituting,

$$2\pi r \gamma \cos \theta = (\pi r^2 h + \frac{1}{3} \pi r^3) \rho g$$

or

$$\gamma = \frac{r \rho g (h + \frac{1}{3} r)}{2 \cos \theta} \quad \dots (II.10)$$

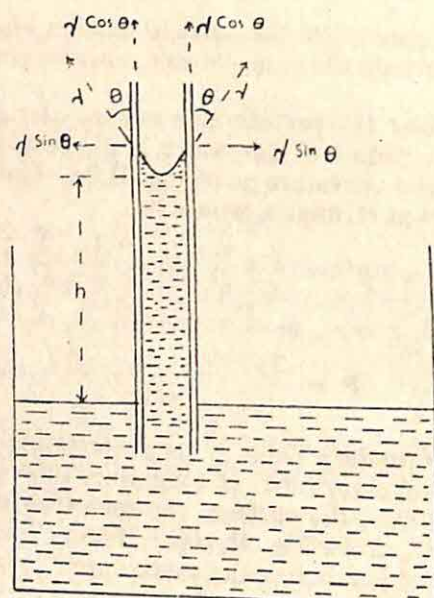


Fig. II.11

Often θ is found to be nearly zero, so that $\cos \theta \approx 1$, hence

$$\gamma = \frac{r\rho g(h + \frac{1}{2}r)}{2} \text{ dynes/cm} \quad \dots \text{ (II.11)}$$

Thus, the measurement of h and r with a knowledge of the density ρ will enable us to determine the surface tension. Various precautions are of course taken in making the measurements.

(b) *Maximum Bubble Pressure Method (Jaeger's method)*: An ingenious method for determination of surface tension is based on the measurement of maximum pressure in an air bubble within the liquid. A long thin glass tube AB with its lower portion ending into a smooth fine capillary is kept vertically immersed into the experimental liquid up to a depth of h_2 cms. The tube is connected to an air reservoir D through a manometer C . On introducing water in reservoir D the pressure rises and the air in the capillary tube AB is slowly forced out in the form of a bubble. Slowly the size of bubble increases and ultimately breaks away. The pressure just before the bubble breaks away is maximum and is noted from the manometer (Fig. II.12.) If the bubble is regarded as a spherical one, the excess pressure inside the bubble due to surface tension would be $\frac{2\gamma}{r}$, where γ is the surface tension and r is the radius of the capillary end. At the moment of breaking, the two opposite pressures are equal. So,

$$P + h_1\rho_1g = P + h_2\rho_2g + \frac{2\gamma}{r}$$

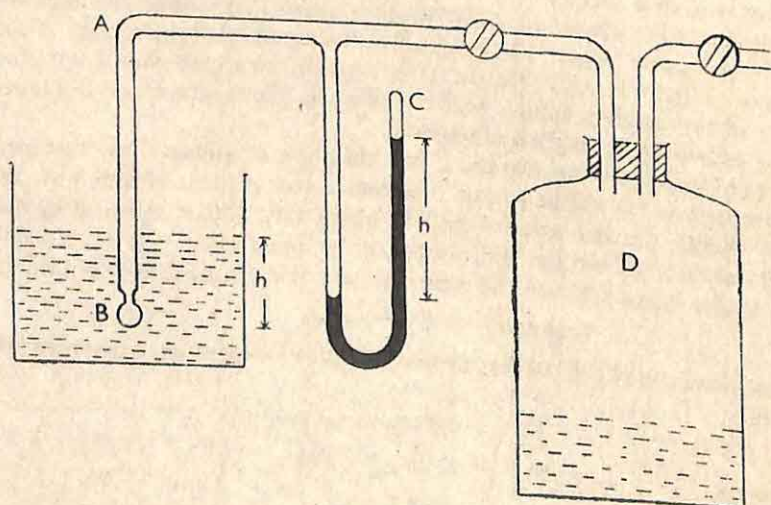


Fig. II.12

$$\text{or} \quad \gamma = \frac{rg}{2} [h_1 \rho_1 - h_2 \rho_2]$$

where P = atmospheric pressure,

ρ_1 = density of manometric liquid,

ρ_2 = density of the experimental liquid,

h_1 = reading of the manometer.

(c) *Drop-Weight Method*: When a drop of liquid is at the point of being detached from the circular end of a vertical capillary tube, the upward and downward forces must balance one another. The upward force is $2\pi r\gamma$. The downward force consists of the weight of the liquid drop and the excess pressure inside the drop, which has a curved surface. The drop at the moment of detachment is considered cylindrical at the mouth. So, the excess pressure inside the drop is $\frac{\gamma}{r}$.

Hence, the total downward force = $mg + \pi r^2 \cdot \frac{\gamma}{r}$. At equilibrium, $2\pi r\gamma = mg + \pi r^2 \cdot \frac{\gamma}{r}$

$$\text{or} \quad \gamma = \frac{mg}{\pi r} \quad \dots \text{ (II.12)}$$

The determination of the weight of a liquid drop and the radius of the capillary mouth would give the desired surface tension. In fact the relation is not so simple. The quantity of the liquid released in a drop depends on various factors. From a careful study of it with liquids of known surface tensions Harkins and Brown have established an empirical relation,

$$\gamma = \frac{mg}{r} \phi$$

where ϕ is a factor depending upon $\frac{v}{r^3}$, v being the volume of the liquid drop. The values of ϕ for tubes of different dimensions have also been tabulated by them.

If ρ denotes the density of the liquid, we may write

$$\gamma = \frac{v\rho}{r} \phi$$

This relation is often used to compare the relative surface tensions of two or more liquids. A pipette-like tube (Fig. II.13), called *Stalagmometer*, having a very smooth capillary end is used for the purpose. The tube is thoroughly cleaned and the experimental liquid is sucked in. The apparatus is kept in a vertical position in an enclosure free from disturbances or air currents. The liquid is allowed to drop very slowly, ensuring that every drop is fully formed. A definite volume of the liquid (say v c.c) determined by marks in the stalagmometer is allowed to come out and the number of drops (n) counted. The density of the liquid is separately determined. Then,

$$\gamma = \frac{\frac{v}{n} \rho}{r} \phi$$

The experiment is repeated with a second liquid whose surface tension γ' is known.

$$\gamma' = \frac{\frac{v}{n'} \rho'}{r} \phi$$

That is,

Since, the same stalagmometer is used and the external factors are unaltered, v and r are the same and ϕ is assumed to be the same, i.e.,

$$\frac{\gamma}{\gamma'} = \frac{n' \rho}{n \rho'} \quad \dots \text{ (II.13)}$$

γ is easily calculated as other quantities are known.

(d) *The Ring Detachment Method (du Nouy)*: This is now a commonly used method for quick determination of surface tension with appreciable accuracy. It is based on measurement of the force P , required to detach a horizontal platinum ring (radius R) from the surfaces of the experimental liquid. The force will be required to overcome the pull due to surface tension. So,

$$P = 4\pi R\gamma, \quad \text{i.e.,} \quad \gamma = \frac{P}{4\pi R} \quad \dots \text{ (II.14)}$$

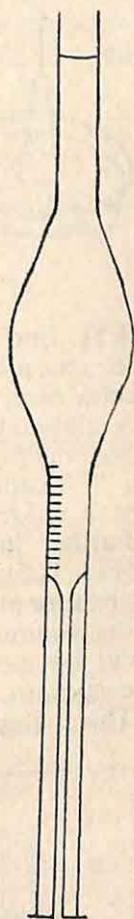


Fig. II.13

To be precise, the relation is to be expressed as $\gamma = \frac{P}{4\pi R} \phi$, where ϕ is Harkins and Jordan correction factor,* which depends on the size of the ring, the thickness of the wire, density of the liquid, etc. The apparatus used is the du Nouy's torsion balance (Fig.14). The Pt-ring is thoroughly cleaned and suspended from the hook of the beam balanced at the other end by the torsion-

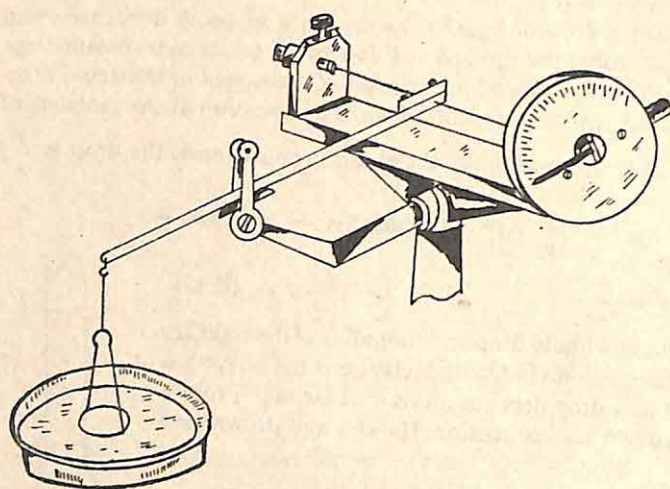


Fig. II.14

wire. One end of the torsion wire carries a pointer on a circular scale and is previously calibrated with known weights taken by the beam. In a flat dish, the liquid is taken and placed in such a way that the Pt-ring just touches the surface. The knob of the torsion wire is then slowly turned until the ring is just detached from the surface, keeping the beam always in horizontal position. The reading of the pointer gives the force P just at the moment of detachment of the ring from the liquid surface. The magnitude of γ is then evaluated from equation (II.14).

II.11. Surface Tension and Vapour Pressure. Surface tension is connected with the attraction between the molecules. The process of evaporation in which the molecules escape from the surface also depends upon the intermolecular attraction. A relation therefore must exist between the vapour pressure and the surface tension. We may proceed to find out the relation in the following way.

A capillary tube is dipped into a liquid and the capillary rise AB is h , when $\gamma = \frac{1}{2}h\rho gr$, where r is the radius of the tube and ρ is the density of the liquid. Further imagine the system is enclosed in a chamber and is in equilibrium (Fig. II.5). There is a vapour pressure difference at A and B . If p be the vapour pressure at B , then the vapour pressure at A is $P - h d g$, where d is the density of the vapour. This must be the maximum vapour pressure in contact with the curved surface at A . If it were not so, then there would have been condensation or evaporation at A , and a circulation would set up without any supply of energy. This is contrary to our experience. The difference of vapour pressure,

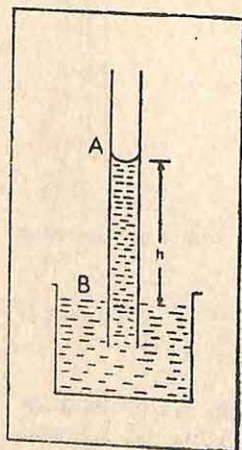


Fig. II.15

$$dp = h d g$$

But we know,

$$h = \frac{2\gamma}{\rho g r}$$

$\therefore$

$$dp = \frac{2\gamma d g}{\rho g r} = \frac{2\gamma d}{\rho r}$$

Assuming ideal gas laws for the vapour, $d = \frac{Mp}{RT}$,

we have,

$$dp = \frac{2\gamma p M}{\rho R T r}, \quad \text{i.e. } \frac{dp}{p} = \frac{2\gamma M}{\rho R T r} \quad \dots (II.15)$$

This is the relation between the surface tension and the vapour pressure.

* J. Am. Chem. Soc. 1930, 52, 1756.

II.12. Surface Tension and Temperature : Eötvös-Ramsay-Shields Relation. It has generally been observed that the surface tension of liquids decreases with rise in temperature. A quantitative relation, though empirical, between surface tension and temperature was given by Eötvös. If M be the molecular weight and v be the specific volume of a liquid, then molar surface of a liquid, assuming it to be a spherical mass, is proportional to $(Mv)^{2/3}$. The molar surface energy is then $k_1(Mv)^{2/3}\gamma$, where γ is the surface tension of the liquid and k_1 is an appropriate constant. Eötvös suggested that the molar surface energy bears a linear relationship to temperature (t), i.e.,

$$k_1(Mv)^{2/3}\gamma = -k_2t + c_1 \text{ (constant)}$$

or

$$(Mv)^{2/3}\gamma = -kt + c \text{ (constant)}$$

Remembering that at the critical temperature t_c the surface tension (γ) is zero, we have, the constant $c = kt_c$

Hence,

$$(Mv)^{2/3}\gamma = k(t_c - t)$$

It follows that if we plot $(Mv)^{2/3}\gamma$ against temperature, the line will meet the temperature-axis at the critical temperature. Ramsay and Shields, however, showed from experimental results with many liquids that the lines actually cut the temperature-axis approximately six degrees before the critical temperature. Eötvös equation was therefore modified to the form, in order to conform to experimental results,

$$(Mv)^{2/3}\gamma = k(t_c - t - 6) \quad \dots \text{ (II.16)}$$

For many liquids, the constant k often called Eötvös-Ramsay-Shields coefficient, has the same magnitude, 2.1. The constant is evaluated by measuring surface tension and specific volume (from density) at two temperatures, for,

$$k = - \frac{\gamma_1(Mv_1)^{2/3} - \gamma_2(Mv_2)^{2/3}}{t_1 - t_2} \quad \dots \text{ (II.17)}$$

In the case of water, alcohol, carboxylic acids, etc., the value of k was found to be less than 2.1 and the value also rises with temperature. This abnormality has been attributed to the associated state of the molecules in these liquids. That is, the value of k is 2.1 for normal liquids, but for the associated liquids the magnitude is less. Ramsay and Shields further suggested that if x molecules be associated to form each unit in the liquid state, i.e., if x be the degree of association, then

$$- \frac{\gamma_1(xMv_1)^{2/3} - \gamma_2(xMv_2)^{2/3}}{t_1 - t_2} = k = 2.1 \quad \dots \text{ (II.18)}$$

from which x the degree of association can be obtained. This relation is only a qualitative one. There are quite a number of non-associated liquids for which the k -value is less than 2.1. On the other hand, many liquids are known having k -values much above 2.1.

Macleod's Equation : Macleod proposed a relation between surface tension and density empirically in the form,

$$\gamma^{1/3}/(D-d) = c \text{ (constant)} \quad \dots \text{ (II.19)}$$

where D = density of the liquid and d = density of the vapour.

This relation can also be arrived at from Eötvös equation and van der Waals equation,

$$(a) \text{ Eötvös : } \gamma \left(\frac{M}{D} \right)^{2/3} = k(t_c - t) = k(T_c - T) = kT_c \left(1 - \frac{T}{T_c} \right)$$

which was modified by Katayama, as

$$\gamma \left(\frac{M}{D-d} \right)^{2/3} = kT_c \left(1 - \frac{T}{T_c} \right) \quad \dots \text{ (II.20)}$$

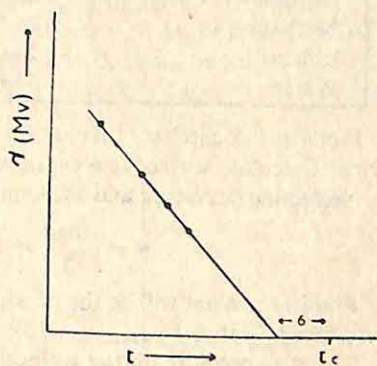


Fig. II.16

$$(b) \text{ van der Waals : } \gamma = \gamma_0 \left(1 - \frac{T}{T_c} \right)^n, \text{ where } n \approx 1.2 \quad \dots (II.21)$$

By combining equations (II.20) and (II.21), we obtain the Macleod's equation (II.19). This relation is obeyed by many organic liquids almost very near to their critical temperatures. We shall see later an important application of Macleod's equation in connection with the determination of the structure of molecules.

The surface tension values of some common liquids are given in the Table below.

SURFACE TENSIONS OF SOME LIQUIDS IN DYNES/CM

Liquids	Temperature (°C)			
	0°	20°	40°	60°
Benzene	31.6	28.9	26.3	23.7
Toluene	30.7	28.4	26.1	23.8
Carbon Tetrachloride	—	26.8	24.3	21.9
Acetone	26.2	23.7	21.2	18.6
Methanol	24.5	22.6	20.9	—
Ethanol	24.05	22.27	20.6	19.01
Water	75.64	72.75	69.56	66.18

Problem : A capillary tube of internal diameter 0.2 mm is dipped into water when water rises 15 cms. Calculate surface tension of water.

Neglecting curvature and assuming that angle of contact is zero,

$$\gamma = \frac{rhdg}{2} = \frac{1}{2} (0.01 \times 15 \times 1 \times 981) = 73.6 \text{ dynes/cm}$$

Problem : What will be the pressure inside an air bubble of 0.1 mm radius situated just below the surface of water. [$\gamma_{\text{water}} = 72 \text{ dynes/cm}$, atm. $p = 1.013 \times 10^6 \text{ dynes/cm}^2$]

The atm. pressure on the surface = 1.013×10^6

$$\text{The excess pressure inside the bubble} = \frac{2\gamma}{r} = \frac{2 \times 72}{0.01} = 0.0144 \times 10^6$$

$$\text{Hence net pressure inside the bubble} = (1.013 + 0.0144) \times 10^6 \frac{\text{dynes}}{\text{cm}^2}$$

Problem : A drop of water, 0.4 cm in radius, is split up into 125 tiny drops. Find the increase in surface energy. [$\gamma_{\text{water}} = 72 \text{ dynes/cm}$]

If r be the radius of the tiny drops, then

$$\frac{4}{3} \pi (0.4)^3 = \frac{4}{3} \pi (r)^3 n = \frac{4}{3} \pi (r)^3 \times 125, \text{ whence } r = 0.08 \text{ cm.}$$

The increase in surface area is

$$4\pi (0.08)^2 \times 125 - 4\pi (0.4)^2 \\ = 4\pi (0.64) \text{ sq. cm}$$

The increase in surface energy = area $\times$ surface tension

$$= 4\pi \times 0.64 \times 72 = 578.6 \text{ ergs}$$

Problem : The limbs of a vertical U-tube have internal diameters of 1 mm and 2 mm respectively. It is partially filled with a liquid of density 0.82 and surface tension 50 dynes. What is the difference in level of the liquid in the two limbs?

Difference of pressure in the two limbs is

$$\frac{2\gamma}{r_1} - \frac{2\gamma}{r} = 2 \times 50 \left[\frac{1}{0.05} - \frac{1}{0.1} \right] = 1000 \text{ dynes.}$$

$$\therefore h dg = 1000$$

$$\text{or } h = \frac{1000}{dg} = \frac{1000}{0.82 \times 981} = 1.24 \text{ cms}$$

VISCOSITY

II.13. Viscosity of Liquids. In section I.38, we have defined the viscosity of liquids as the property which opposes the relative motion of adjacent layers. It is indeed

a kind of internal friction. We have also defined the *coefficient of viscosity* (η) there as the tangential force per unit area required to maintain unit difference of velocity between two layers unit distance apart. It is expressed in dynes sec per sq. cm. Poiseuille's equation (I.76).

$$\eta = \frac{\pi(P_1 - P_2)r^4}{8L \left(\frac{\partial v}{\partial t} \right)} \quad \dots (I.76)$$

is the basis of most of the methods employed for the determination of coefficient of viscosity. We shall briefly mention here the outline of some of the methods.

(i) *Measurement of Absolute viscosity.* If v volume of a liquid flows slowly through a capillary tube of radius r and length l in time t under a constant pressure-head p , then the Poiseuille's equation may be written as,

$$\eta = \frac{\pi p r^4 t}{8lv} \quad \dots (II.22)$$

The knowledge of radius and length of the tube and determination of volume of liquid passing in a given time under a known pressure-head would give us the viscosity. This can be conveniently done in Koch's apparatus shown in Fig. II.17. Tubes x , y and z have the same radius σ . The liquid in x is allowed to fall from a_1 to a_2 and it flows through the horizontal capillary tube M of length l . The level in z rises from b_1 to b_2 . The time required is measured, say θ seconds.

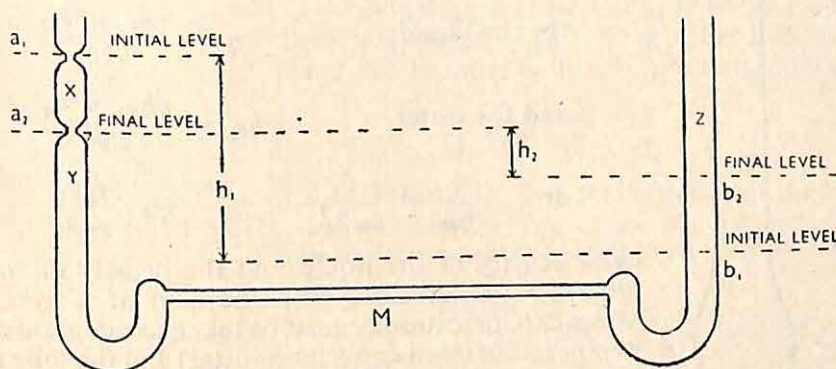


Fig. II.17. Koch's apparatus for determination of viscosity

If we assume that in a small time-interval $d\theta$ seconds, dv c.c. of liquid flow through the capillary tube, then applying equation (II.22), we have

$$dv = \frac{\pi P r^4 d\theta}{8l\eta} = \frac{\pi h \rho g r^4}{8l\eta} d\theta$$

where ρ is the density of the liquid, and r is the radius of the capillary. But we know,

$$dv = -\pi \sigma^2 \frac{dh}{2}, \text{ i.e., } v = \pi \sigma^2 \frac{h_1 - h_2}{2} \quad \dots (I)$$

Hence,
$$-\pi \sigma^2 \frac{dh}{2} = \frac{\pi h \rho g r^4}{8l\eta} d\theta$$

$$\therefore \frac{\sigma^2}{2} \ln \frac{h_1}{h_2} = \frac{g \rho r^4 \theta}{8l\eta}$$

Hence,
$$\eta = \frac{2g \rho r^4 \theta}{8l \sigma^2 \ln \frac{h_1}{h_2}} \quad \dots (II)$$

Substituting (I) in (II),

$$\eta = \frac{\pi(h_1 - h_2)g\rho r^4\theta}{8lv\ln \frac{h_1}{h_2}}$$

The quantities on the right hand side being measured, the value of η is known. It should be remembered that the flow through the capillary must be a slow streamline one without any turbulence. There must not be any slip at the surface of the capillary.

(ii) *Relative viscosity.* It is often quite convenient to determine the relative viscosity of a liquid, say with respect to water. The absolute viscosity of water has been determined very accurately at various temperatures. We can thus easily obtain the true viscosity of a given liquid. The relative viscosity for ordinary liquids is commonly determined with the help of the Ostwald viscometer. It consists of a tube as shown in Fig. II.18.

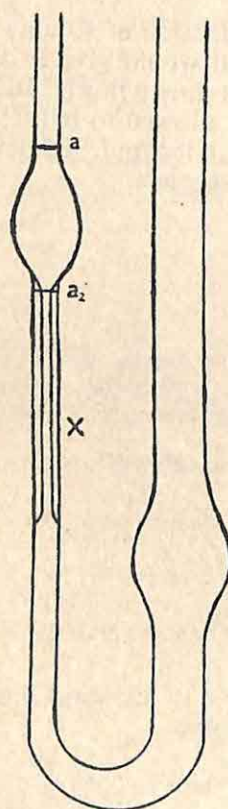


Fig. II.18

The bulb in the wider limb of the tube is first filled with the liquid and the liquid is then sucked up in the narrower limb up to the level a_1 . The liquid then flows down the capillary X and the time θ_1 required to fall from level a_1 to a_2 is carefully noted. The experiment is repeated with water in the same tube and the corresponding time (θ_2) is also noted. Obviously,

$$\text{for the liquid,} \quad \eta = \frac{\pi h \rho_l g r^4 \theta_1}{8lv}$$

$$\text{and for water,} \quad \eta_w = \frac{\pi h \rho_w g r^4 \theta_2}{8lv}$$

$$\text{or} \quad \frac{\eta}{\eta_w} = \frac{\rho_l \theta_1}{\rho_w \theta_2}, \quad \text{or} \quad \eta = \eta_w \cdot \frac{\rho_l \theta_1}{\rho_w \theta_2}$$

The density of the liquid and the density of water are separately determined with the help of a pycnometer. Adequate precautions must be taken to maintain constant temperature (by using a thermostat) and the tube must be thoroughly cleaned before use.

The relative viscosity may also be determined by several other methods, only two of which are briefly mentioned below.

Falling sphere viscometer. When a body moves through a viscous medium its motion is opposed by the frictional resistance. In order to maintain a uniform velocity, a driving force is applied to overcome the viscous drag. It was shown by Stokes that when a spherical body of radius r moves with a constant terminal velocity u through a medium having coefficient of viscosity η , then the driving force (f) which just balances the frictional resistance is given by the relation,

$$f = 6\pi\eta ru \quad \dots (II.23)$$

If the spherical body falls under gravity, then we know,

$$f = 4/3\pi r^3(d - d_l)g$$

where d and d_l are the densities of the solid sphere and the liquid respectively.

$$\text{Hence,} \quad 6\pi\eta ru = 4/3\pi r^3(d - d_l)g$$

$$\text{or} \quad u = \frac{2}{9} \frac{r^2(d - d_l)g}{\eta} \quad \dots (II.24)$$

This is Stoke's law.

Evidently if we can measure the velocity of a spherical ball moving down through a vertical column of the liquid, it would be easy to know the viscosity of the medium.

An apparatus of the type shown in Fig. II.19 is used for the purpose. The tube is filled with the liquid under investigation. Small steel balls, having diameter of 2-3 mm. are dropped through the narrow opening at *B*. The time θ taken by a ball to travel from a_1 to a_2 is noted by a stop watch. The velocity (u) is given by length a_1a_2/θ . The coefficient of viscosity is then calculated from the equation (II.24). The tube *A* is kept in a large cylinder of water provided with a thermometer and a stirrer to maintain constant temperature.

The walls of the tube however influence the velocity and a correction term is employed for the same in the form

$$u = \frac{2}{9} \frac{r^2(d-d_l)g}{\eta \left(1 + 2.1 \frac{r}{R}\right)} \quad (\text{II.25})$$

where R is the radius of the container-tube.

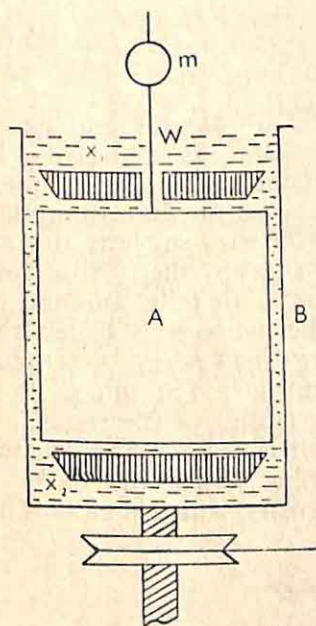


Fig. II.20

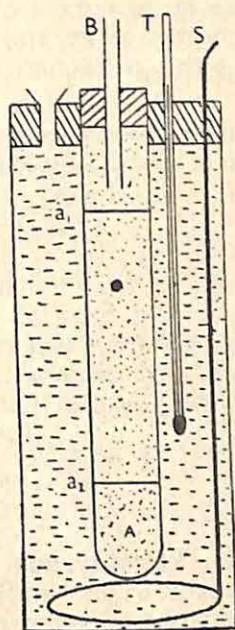


Fig. II.19

When the relative viscosity is determined by this method, times of fall of the same steel ball through the two liquids, θ_1 and θ_2 , are determined. Then,

$$\frac{\eta_1}{\eta_2} = \frac{d-d_{l1}}{d-d_{l2}} \cdot \frac{\theta_1}{\theta_2} \quad \dots (\text{II.26})$$

where d_{l1} and d_{l2} are the densities of the two liquids, —experimental one and the reference one. The method is suitable for liquids which are comparatively more viscous, such as castor oil.

Rotating cylinder method : Hatschek viscometer. In this method the liquid is taken in between two concentric cylinders *A* and *B* (Fig. II.20). When one of the cylinders is rotated, say the outer cylinder *B*, with a constant angular velocity, there is shearing of the liquid and it drags the inner cylinder with it until the twist of the suspension wire neutralises the same. The deflection (Δ), noted by a mirror (*m*) and a scale, is proportional to η and to u , the velocity.

$$\text{That is,} \quad \Delta = k\eta u$$

$$\text{The relative viscosity then, } \eta_1/\eta_2 = \frac{\Delta_1}{\Delta_2}$$

The method gives satisfactory results for liquids of high viscosities.

The viscosities of some common liquids are given in the Table below.

VISCOSITIES IN MILLIPOISES AT 20°C

Water	10.05	Chloroform	5.63
Ethanol	11.94	Carbon Tetrachloride	9.58
Methanol	5.93	Chlorobenzene	6.37
Acetone	3.31	Nitrobenzene	19.8
Ethyl ether	2.45	Benzene	6.47
Acetic acid	12.22	Glycerine	10690

The measurement of viscosity has become indispensable in the study of biology and physiology, and also in dealing with various problems of technology, specially in paint, petroleum, ink, colloids, rubber, textiles, etc.

Problem : Heptane (density 0.7) flows through a viscometer in 63 seconds while same volume of water requires 108 seconds at 20°C. Calculate the absolute viscosity of heptane if that of water is 0.01005 poise.

$$\frac{\eta}{\eta_w} = \frac{d \cdot \theta}{d_w \cdot \theta_w} = \frac{0.7 \times 63}{1 \times 108}$$

$$\therefore \eta = \frac{0.7 \times 63}{108} \times 0.01005 = 0.00503 \text{ poise}$$

Problem : A steel ball of density 7.9 and diameter 4 mm took 50 seconds to fall a distance of 1 metre through an oil of density 1.1. Calculate the viscosity of the oil.

Using equation II.24, we have,

$$\eta = \frac{2}{9} \cdot \frac{r^2(d-d_l)g}{u} = \frac{2}{9} \cdot \frac{(0.2)^2(7.9-1.1) \times 981}{\frac{100}{50}} = 29.65 \text{ poise}$$

II.14. Viscosity and Temperature. Viscosities of liquids decrease with rise in temperature as shown in the Table below. Different empirical relations between viscosity and temperature have been suggested. The relation which has been found quite satisfactory for a considerable number of liquids is expressed in the form,

$$\log \eta = \frac{a}{T} + \beta \quad \dots \text{ (II.27)}$$

where a, β are constants for the given liquid.

Temperature has different effects on the viscosities of liquids and gases. It means that the cause of viscosity in gases is not the same as in liquids. In Sec. 1.40 the viscosity in gases has been explained. For the viscosities in liquids different theories have been proposed which are often based on the assumption that liquids possess a certain structure. One of these theories suggests that in order to take part in the liquid flow a molecule must push away the surrounding molecules. To achieve this the molecule must acquire a definite amount of necessary energy. This energy (A) per mole, above the average, is called the energy of activation. The number of molecules having this energy is proportional to the factor $e^{-A/RT}$ given by Maxwell-Boltzmann law. The rate of flow then depends upon this number. In other words, the viscosity or the resistance to the flow of liquids would be proportional to $e^{A/RT}$. It is obvious that higher the value of A , greater will be the viscosity. On the other hand, with increase in temperature, $e^{A/RT}$ will decrease and hence the viscosity will decrease. The viscosity is thus $\eta = B \cdot e^{A/RT}$, i.e.,

$$\log \eta = \frac{A}{RT} + \log B = \frac{a}{T} + \beta$$

which is the same as the experimentally observed empirical relation given by equation (II.27). There are several other theories proposed to explain the viscosity in liquids, the discussion of which is beyond the scope of the text.

VISCOSITY OF LIQUIDS AT DIFFERENT TEMPERATURES IN POISES

	0°	20°	40°	60°C
Water	0.0179	0.01005	0.0065	
Ethyl alcohol	0.0177	0.0112	0.0072	0.0047
Benzene	0.0090	0.0065	0.0049	0.0065
				0.0039

The reciprocal of viscosity is called *fluidity*, $\phi = 1/\eta$. Fluidity is defined as the measure of the tendency of flow of a liquid, while viscosity is a measure of

the resistance offered to its flow. When two non-associated non-polar liquids are mixed, the fluidity becomes additive. Thus $\phi = \alpha_1\phi_1 + \alpha_2\phi_2$. . . (II.28) where α_1, α_2 are the mole-fractions of the two liquids. Kendall has suggested instead the relation

$$\log \phi = \alpha_1 \log \phi_1 + \alpha_2 \log \phi_2 \quad \dots (II.29)$$

These relations, however, fail in the case of liquids which are associated or which interact.

II.15. Molecular Weight from Viscosity. The viscosity measurements have been utilised recently in the determination of molecular weight of polymers. The addition of polymer molecules to a solvent increases the viscosity. If η_0 and η denote the measured viscosity coefficients of the pure solvent and the solution respectively, then η/η_0 is called the relative viscosity. Several other functions, correlating the increased viscosity to the properties of the solute, are also derived.

$$\text{Specific viscosity} \quad \eta_{sp} = \frac{\eta - \eta_0}{\eta_0}$$

$$\text{Reduced specific viscosity} = \frac{1}{C} \left[\frac{\eta - \eta_0}{\eta_0} \right], \text{ where } C = (\text{conc.})$$

$$\text{Intrinsic viscosity, } [\eta] = \lim_{C \rightarrow 0} \frac{1}{C} \left[\frac{\eta - \eta_0}{\eta_0} \right]$$

The intrinsic viscosity represents the fractional change in the viscosity of a solution per unit concentration of polymer at infinite dilution.

It has been possible to obtain an empirical relation between the intrinsic viscosity of the solution and different molecular-weight fractions of the polymer in the form $[\eta] = KM^a$

$$\text{or} \quad \log [\eta] = a \log M + \log K \quad \dots (II.30)$$

where K and a are constants depending on the solvent and the polymer, and also on the temperature.

The intrinsic viscosity is obtained by extrapolation to infinite dilution of the measured reduced specific viscosities. Calibration measurements of viscosities of solutions containing polymer fractions of known molecular weights allow K and a to be evaluated. The value of a which is often 0.6 to 0.7, may increase to 1 to 2, depending upon the shape of the polymer molecule. With the knowledge of the values of the empirical constants, the measurement of viscosity easily yields the molecular weight of any batch of polymer using eqn. (II.30). See also Sec. XVI.11.

REFERENCES FOR FURTHER READING

1. A treatise on physical chemistry, Vol II—Glasstone & Taylor
2. Fluidity and plasticity—Bingham.
3. Kinetic theory of liquids—Frenkel.
4. Viscosity of liquids—Hatschek.

Problems

1. Deduce an expression for the lowering of mercury surface when a glass tube of internal radius r is inserted. What will be the depression if $r = 1 \text{ mm}$?
Given $\gamma(\text{Hg}) = 520 \text{ dynes/cm}$, density = $13.6 \text{ gm/c.c. at } 25^\circ\text{C}$.
2. Benzene at 20°C rises 4.07 cms in a capillary tube of radius 0.0165 cm. Calculate the surface tension of benzene if its density be 0.88.
3. How high will water rise in a capillary tube of diameter $1 \times 10^{-2} \text{ cms}$ if the surface tension be 72.75 dynes/cm. [Ans : 29.7 cms]

4. For CCl_4 , the densities and surface tensions are

temp	density	surface tension
80°C	1.477	18.70
150°C	1.322	11.20

Calculate the value of k in Ramsay-Sheilds equation and thence the critical temperature of CCl_4 .

5. A mist particle has a mass 10^{-12} gms. Show that its vapour pressure at 20°C is 1.002 times that of water.

6. The heat of vaporisation of ether (b. pt. 35°C) is 88.4 cal/gm. What is the boiling point at 750 mm? What is the vapour pressure at 36 mm?

7. The thermal pressure coefficient for CCl_4 is 11.7 atm/degree at 20°C and 1 atmosphere. Calculate the internal pressure. (Use eqn. II.6).

8. The viscosity of $\text{C}_6\text{H}_5\text{Cl}$ (b. pt. 132°C) is 0.799 centipoise at 20°C. Estimate its viscosity at 100°C.

9. A droplet of water (radius 10^{-3} cm) is falling in air at 20°C (viscosity, 1.808×10^{-4}). What will be the velocity of its fall?

10. The densities of water and acetone at 20°C are 0.9982 and 0.792 gms/c.c. respectively. The viscosity of water at 20°C is 1.005×10^{-2} poise. If water requires 120.5 sec to run down a viscometer tube and acetone requires 49.5 sec, calculate viscosity of acetone.

11. At 20°C, the time of flow in a viscometer (Ostwald) and the densities of benzene and alcohol are

	density (gm/c.c.)	Time of flow (sec)
benzene	0.8794	183
alcohol	0.7893	378

find out the viscosity of alcohol if that of benzene be 6.47 millipoise. [Ans : 1.2×10^{-2} poise]

12. A steel ball of density 8.0 gm/c.c. and radius 2 mm is found to fall with a velocity of 1.0 cm/sec. in a liquid of density 1.8 gm/c.c. What is the viscosity of the liquid. [Ans : 54.0 poise]

THE SOLID STATE

Solids are characterised by their definite shape and also their considerable mechanical strength and rigidity. The rigidity is due to the absence of the translatory motion of the structural units (atoms, ions etc.) of the solid. These units remain fixed to a mean position about which they may vibrate. The forces of attraction between these units are quite large.

Solids are generally classified as crystalline or amorphous. In a crystalline solid, the atoms are arranged in a definite pattern constantly repeated. In consequence the crystalline solid has a definite geometrical configuration, characteristic of the nature of the substance. The crystals often have a plane fracture and they also have sharp melting points. The amorphous solids have no definite geometrical form and are regarded as supercooled liquids with high viscosity. The amorphous solids have conchoidal fracture and they melt slowly over a range of temperature. We shall deal in this chapter with the phenomena associated with the crystalline solids.

III.1. Crystals. Crystals are bounded by surfaces which are usually planar and arranged on a definite plan which is an expression of the internal arrangement of the units. The surfaces referred to are called *faces* and where two faces intersect an *edge* is formed. The angle between the normals to the two intersecting faces is the *interfacial angle*. A crystal grows from melt or a solution or from gaseous state by the deposition, on to its faces, of atoms or ions. If these units are deposited preferentially on a certain face, this face will not extend rapidly in area compared to other faces. The faces with larger areas have a slower rate of deposit of atoms or ions. The study of the definite geometrical forms and properties of the crystalline solids is termed *crystallography*. It is however necessary to be first acquainted with three basic laws regarding the forms of the crystals, all derived from their external nature. These laws are :

- (i) *Steno's Law of the constancy of interfacial angles.*
- (ii) *Haüy's Law of rational intercepts.*
- (iii) *Law of constancy of symmetry.*

Steno's Law : It states that *the angles between the corresponding faces on various crystals of the same substance are constant*. It is often seen that the crystal faces are unequally developed, leading to various shapes of the crystals. But the angle of intersection of two corresponding faces will always be the same for any crystal of the same substance. In Fig. III.1, two crystals are represented in two dimensions. The shapes are different but the angles remain the same. The external form or *habit* depends upon the rate of deposition of atoms or ions on the different faces. Thus, sodium chloride crystallises as cubes from aqueous solution and as octahedra from urea solution.

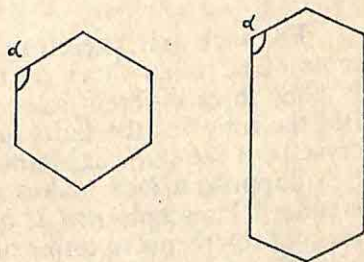


Fig. III.1

Haüy's Law : In 1784, Haüy proposed that the regular external form of crystals was a reflection of the inner regular order of the arrangement of the building units. This indeed is the foundation of crystallography and the basis of crystal systems. The idea of Haüy was confirmed more than a century later when the internal arrangement of atoms became known from X-ray diffraction studies.

A crystal is therefore made up of innumerable smaller crystals. If a crystal is suitably and continuously divided, we shall obtain smaller and smaller crystals,

each of which would be the replica of the original one. In this way a point would be reached, when the smallest possible crystal would appear. Any further breaking would lead to wandering molecules. This smallest crystal is the building unit, more generally called the *unit cell*.

This concept of ordered existence of constituent atoms within led Haüy to establish the *law of rational intercepts* which may be understood in the following way. For describing the geometry of a crystal usually three non-co-planar coordinate axes are taken. These are called crystallographic axes and are selected arbitrarily. They may coincide or be parallel to the edges between the principal faces of the crystal. The axes may be mutually at right angles to one another or may be at some other desired angle. Any face of the crystal will cut one or more of the axes, the face being extended if necessary. Now choose one of the faces which intersects the three axes as the standard. The distances of the points where the standard face cuts the three axes from the origin are called intercepts. Suppose the intercepts made by this face on the three axes are a , b , and c (Fig. III.2). Now if any other face cuts the three axes with intercepts x , y and z , then

$$x : y : z = ha : kb : lc$$

where h , k and l are simple small integers (1, 2, 3, etc.). That is, all faces cut a given axis at distances from the origin which bear a simple ratio to one another. This is the law of rational intercepts.

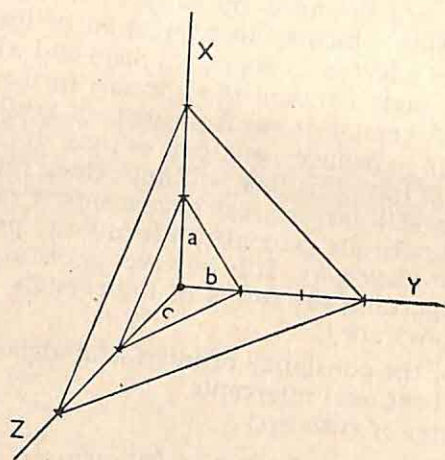


Fig. III.2

For each axis, therefore, there is a unit of length in terms of which the intercepts of all other faces on that axis can be expressed as small whole numbers. For the three different axes of the crystal this unit may or may not be the same. But the ratios of the units ($a : b : c$) on the different axes will be the same for all crystals of the same substance.

Suppose a face makes intercepts x' , y' and z' on the three axes where the standard intercepts are a , b and c , such that $x' : y' : z' = 2a : b : 2c$ then the ratio of intercepts in terms of the standard is $2 : 1 : 2$.

These ratios characterise and represent any plane of the crystal. The coefficients are called *Weiss indices* of the plane. If, however, the plane is parallel to one axis, say z -axis, then the plane will cut the z -axis at infinity. The ratio of intercepts would then be $x' : y' : z' = 2a : b : \infty$. In such cases the use of Weiss indices is rather awkward and so these indices have now been universally replaced by *Miller's indices*. Miller indices are obtained by taking the reciprocals of the coefficients of a , b and c and when necessary the ratio is to be multiplied by the least common multiple to obtain integral values. Thus, Miller indices of the plane mentioned above ($2a : b : 2c$), will be $\frac{1}{2} : 1 : \frac{1}{2}$ i.e., $1 : 2 : 1$. This plane or face is simply indicated as (121).

Similarly a plane perpendicular to one axis and parallel to the other two, having intercepts $a : \infty b : \infty c$ will have indices, as

$$1 : \infty : \infty \text{ (Weiss)}$$

and

$$1 : 0 : 0 \text{ (Miller) i.e., 100-plane.}$$

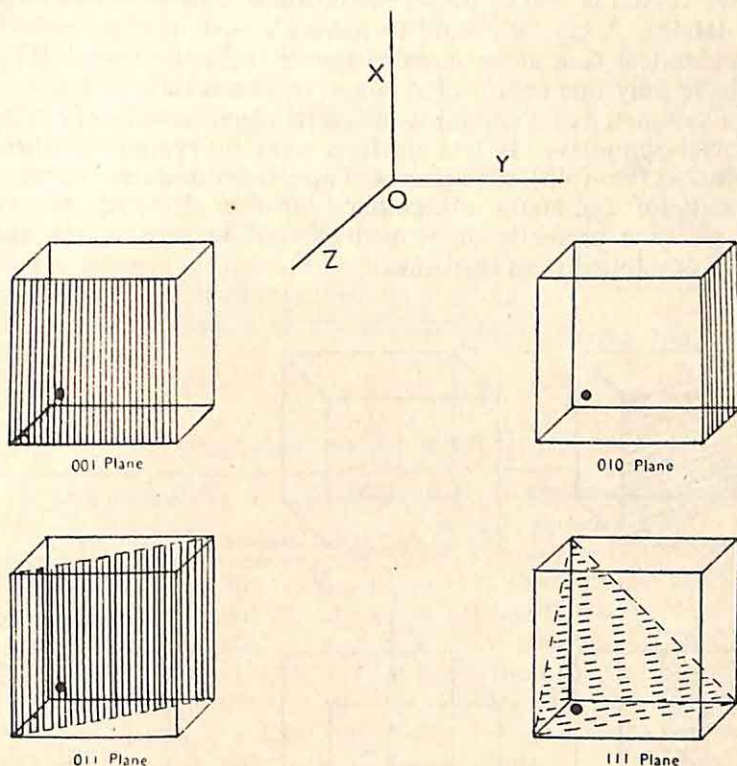


Fig. III.3

If the plane makes an intercept on the negative side, say, $a : -b : \infty c$ the Miller indices for the plane would be $\bar{1}10$, the bar above would indicate intersection of the plane on the negative side of the axis. The symbol $\bar{1}$ means minus unity.

The law of rational intercepts may then be stated as "For any crystalline species, there is a set of axes in terms of which all naturally occurring faces have reciprocal intercepts proportional to small integers (hkl)." The Miller notations of some of the faces in a cubic crystal and in an octahedron are given in Fig. III.3. The eight faces of the octahedron will have Miller indices $111, \bar{1}11, 1\bar{1}1, 11\bar{1}, \bar{1}\bar{1}1, \bar{1}1\bar{1}, 1\bar{1}\bar{1}, \bar{1}\bar{1}\bar{1}$, the axes taken mutually at rt. angles with origin at the centre of the crystal.

The law of symmetry : Most of the crystals present some symmetrical features before our eyes. Symmetry in crystals may be with respect to a plane, a line or a point. A crystal is said to have a *plane of symmetry* when it is divided by an imaginary plane into two halves such that one is the mirror image of the other (Fig. III.4a). A crystal possesses a *line of symmetry* when it is possible to draw an imagi-

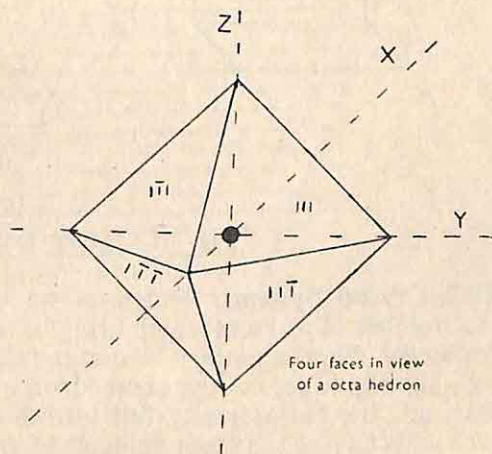


Fig. III.3a. Four faces in view of an octahedron

nary line through the centre of the crystal and then revolve the crystal about this line through 360° in such a way that the crystal appears unchanged more than once. In fact it is possible to have crystals which appear the same two, three, four or six times during one complete revolution of 360° . The line is called the *axis of symmetry*. Depending on the number of times the crystal appears unchanged on revolution, the crystal is said to possess two, three, four and six-fold axes of symmetry (Fig. III.4b). A crystal is said to have a *centre of symmetry*, if every face has another identical face at an equal distance from the centre (Fig. III.4c). A crystal can have only one centre of symmetry. The total number of planes, lines and centre of symmetry of a crystal is called its *elements of symmetry*. The cube has the greatest symmetry. It has thirteen axes of symmetry (three four-fold, four three-fold, six two-fold), nine planes of symmetry and one centre of symmetry, i.e., 23 elements of symmetry altogether. All the elements of symmetry are discernible only in a perfectly developed crystal. In most cases however some faces are more developed than the other.

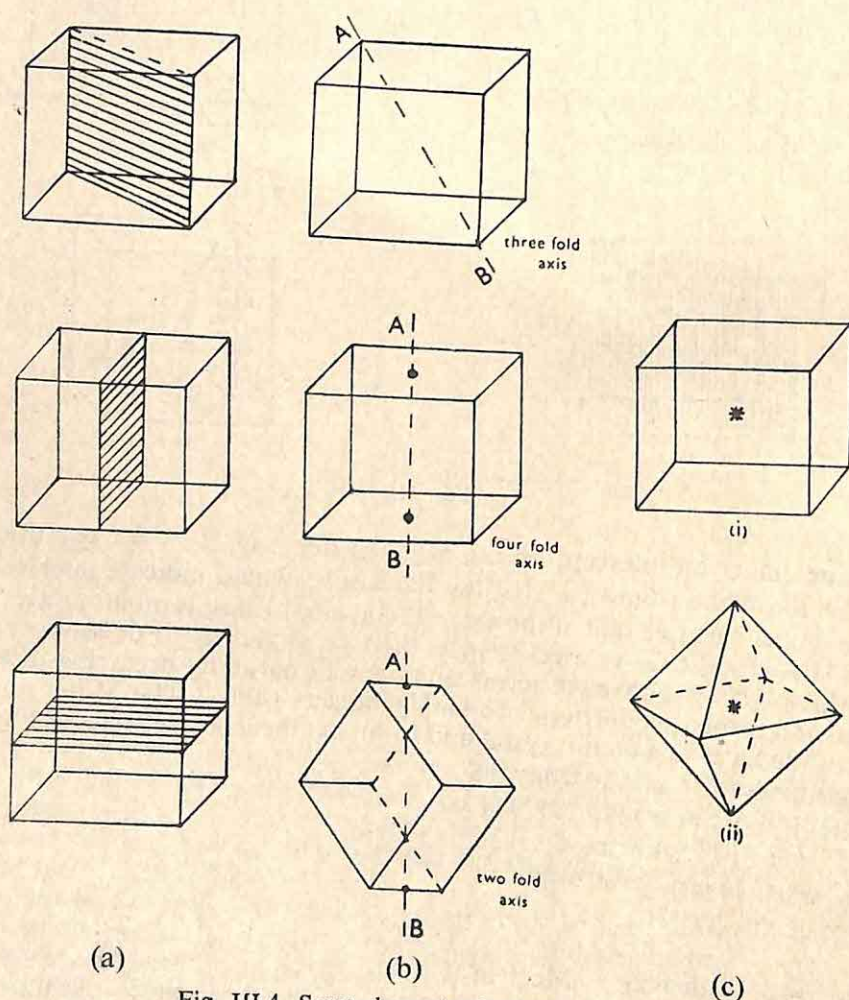
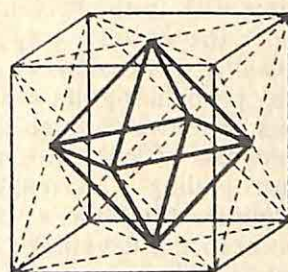


Fig. III.4. Some elements of symmetry in crystals

III.2. Crystal Systems. Whenever we observe a crystal, we find a definite array of a number of its faces which brings to our mind immediately the existence of some symmetry. Such a pattern or combination of faces is called the *form* of a crystal, e.g., the eight faces of the octahedron or the six faces of a cube. It has been found that all the forms really fall into thirty-two *classes* (also called *point-groups*), each class having the same elements of symmetry, i.e., same axes, planes and centre of symmetry. In fact there are only 32 theoretically possible combinations of the elements of symmetry.

On the other hand, based on the axes of reference to represent their faces, the 32 classes can be conveniently grouped into seven *systems*. The crystals belonging to any one system may differ in shape or form, size, elements of symmetry etc., but their axial ratios as also the axial angles will always be the same ; for example, an octahedron is a cube with exclusive growth of 111 plane. The characteristics of the seven systems are given in the table below. The intercepts on the three axes are denoted by a , b and c and the axial angles by α , β and γ . Of the seven systems, the cubic system with rt-angled axes and equal axial intercepts is the most highly symmetrical.

The external shape or *habit* of a crystal is often derived from a modification of the original primitive form. This occurs by *truncation* when an edge between two similar faces is replaced by a plane equally inclined to them or a corner is replaced by a plane. An illustration of the formation of an octahedron is indicated in the diagram.



(b) The octahedron

Fig. III.5. Octahedron

THE SEVEN CRYSTAL SYSTEMS

System	Axial angles	Axial ratios	Minimum symmetry	Example
Cubic	$\alpha = \beta = \gamma = 90^\circ$	$a = b = c$	2 three-fold axes	NaCl, Ag, diamond
Tetragonal	$\alpha = \beta = \gamma = 90^\circ$	$a = b \neq c$	1 four-fold axis	Sn, SnO_2
Orthorhombic	$\alpha = \beta = \gamma = 90^\circ$	$a \neq b \neq c$	2 two-fold axes	BaSO_4 , KNO_3
Monoclinic	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	$a \neq b \neq c$	1 two-fold axis	Gypsum
Rhombohedral	$\alpha = \beta = \gamma \neq 90^\circ$	$a = b = c$	1 three-fold axis	NaNO_3 , ice, Sb
Hexagonal	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$a = b \neq c$	1 six-fold axis	Graphite, Quartz, Zn
Triclinic	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$a \neq b \neq c$	none	$\text{K}_2\text{Cr}_2\text{O}_7$, Blue vitriol

III.3. Crystal Lattices. The idea of lattice developed from the internal regularity suggested from the external appearance of the crystal. A lattice is an infinite set of points repeated regularly through space. A set of points that are repeated at a distance ' a ' along a line is an one-dimensional lattice. The identical equally spaced light posts along a street will be an example. The characteristic of this lattice is that every point (of light-post) is identical with any other such point and that the distance between any two points of posts would be an integral multiple of ' a ' (Fig. III.6a).

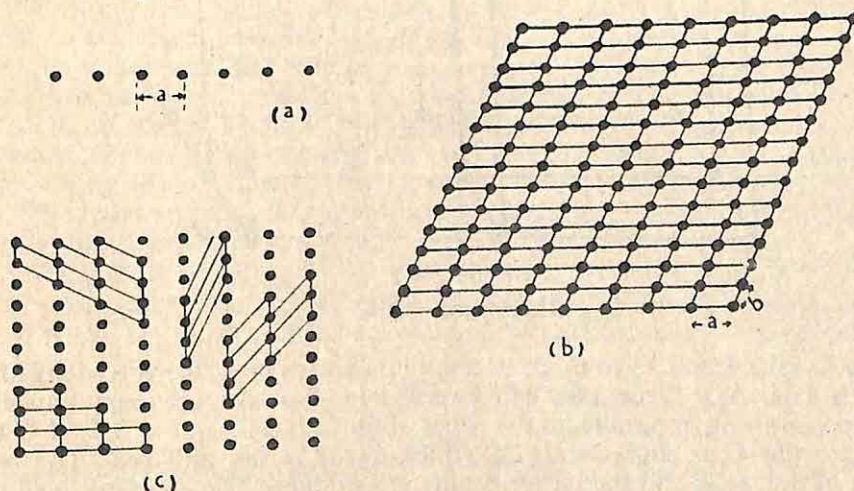


Fig. III.6a. One dimensional lattice

Fig. III.6b and 6c. Two dimensional lattice

When a set of points occurs regularly in a plane, it would constitute a two dimensional lattice. In a tea-plantation or in a printed wall-paper for example, we shall see such two-dimensional lattices. In a tea-garden, if some equidistant plants are chosen in any row and parallel lines are drawn through them in two directions arbitrarily, the whole garden will be divided into a large number of identical parallelograms (Fig. III.6b). It is immaterial which particular plant you start with in the beginning. The size and shape of the parallelograms will depend upon the arbitrary way you choose to draw the parallels (Fig. III. 6c). Similarly, in a wall-paper design, we have the same pattern printed at regular intervals. Choose any particular point of the pattern and mark the same in all the patterns. If parallels be drawn through these marks in any two directions, the wall-paper will be a network of parallelograms. And all similar lattice points will have the same surroundings. The lengths of the sides of the parallelograms, ' a ' and ' b ' are called *primitive translations*. It is easy to understand that any displacement from one point to another similar point can be expressed in terms of ' a ' and ' b ' and the angle between the sides of the parallelogram (Fig. III. 6b).

The method followed in two dimensions may be extended in three dimensions. When the points are regularly repeated in three dimensions, the three-dimensional lattice or space-lattice is obtained. If similar points be connected by sets of parallel lines in three non-coplanar directions as in Fig. III. 6d, the space lattice will be divided into a large number of rhombs or *unit cells*, all identical. Every similar point in the space-lattice will have the same environmental condition. The pattern or shape of the unit cell will of course depend upon the way we connect the points. If the points in space lattice be replaced by identical atoms (or ions), we obtain a crystal structure. The lattice is an array of points ; in the crystal each point is substituted by an atom (or ion). To describe a unit cell or any lattice point, we

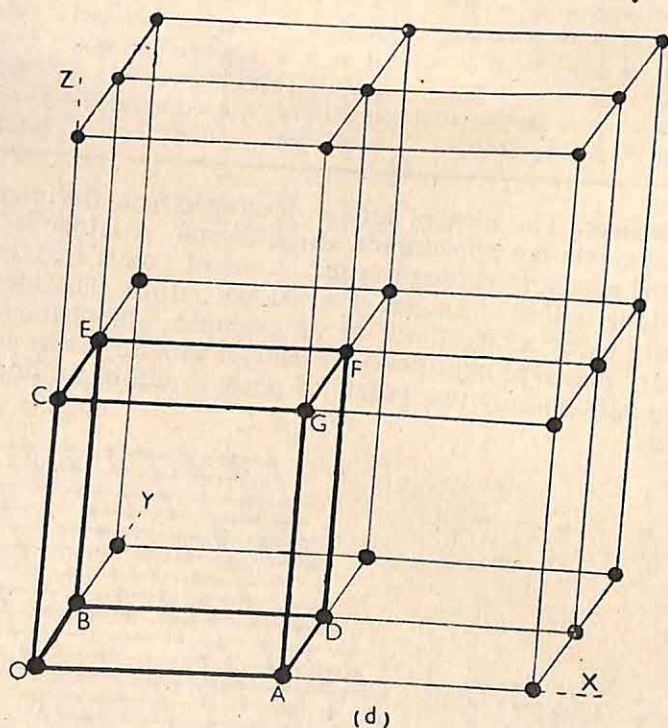


Fig. III.6d. Space lattice

shall have to take recourse to three non-coplanar axes in space with defined units along each axis. Any three axes can be selected, but, for obvious convenience, axes are chosen along or parallel to the edges of the unit cell. In Fig. III.6d, OX , OY and OZ are the axes, and $OADFEC$ (thick-lined) is the unit cell. The regular repetition of unit cells and the lattice points are evident. The edges of the unit cell may not be equal. The lengths of these edges, with the inclinations of the axes

describe the unit cell. The vectors a , b , c are the *primitive translations* in terms of which the position of any other point or sets of points can be described.

A glance at Fig. 5d will reveal that quite a number of lattice-points occur in one or another plane. In fact, the lattice-points may be arranged in many ways in a series of equidistant parallel planes. These are lattice planes. The crystal faces really correspond to lattice-planes. The more common faces of the crystal are those lattice planes where the density of lattice-points are relatively very high. Thus, in Fig. III.5e, we have a section of a space lattice in two dimensions (XY -plane), having axes OX and OY , and the primitive translations are ' a ' and ' b '. Suppose the third axis OZ is at right angles to this plane *i.e.*, perpendicular to the plane of the paper. A cursory glance shows that the lattice planes which will have the largest number of lattice points will be parallel to axes OX and OY *i.e.*, planes like AA or BB , so these are the likely faces of the crystal.

Now, the planes parallel to AA cut the X -axis at certain integral values of ' a ' and will meet the other two axes at infinity. The ratio of intercepts then is $a : \infty : \infty$ *i.e.*, these are, according to Miller indices, (100) planes. The planes parallel to BB cut the Y -axis at integral distances of ' b ' and will meet other axes at infinity. The Miller indices of such planes would be (010).

The plane PQ and its parallels will make intercepts equal to ' a ' and ' b ' on the two axes and will be parallel to the Z -axis. The Miller indices of such planes are (110). Likewise, the planes RS and VW will be (320) and (410) planes. These last mentioned planes contain a fewer number of lattice-points and are not likely to appear as crystal faces normally. In any case, the lattice-concept leads to the expression of faces in terms of rational intercepts. The law of Haüy is thus established.

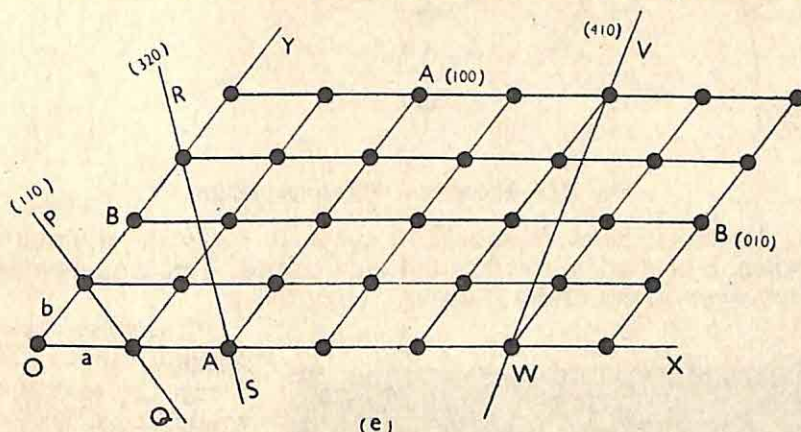


Fig. III.5e Lattice planes

III.4. Crystals and X-rays. In the first decade of this century it was realised that X-rays are really light waves of very short wave-lengths probably of the order of $10^{-8} \sim 10^{-9}$ cms. This however could not be established by diffraction experiments as it was not possible to prepare a grating with about 10^8 lines per centimetre. During those days, the crystals were also believed to be constituted by orderly arrangement of atoms or ions in space lattices. Some rough estimates had set the distances between atoms in crystals at about 10^{-8} cms. One such approximate calculation may be shown here. Take a gm-mole of a substance having mol. wt. M and density d and suppose it is present in the form of a cube. The side (x) of the cube containing 1 gm-mole would be, $x = (M/d)^{1/3}$.

Assuming that the atoms of the substance are present in simple cubic lattice, the number of atoms occurring along any edge of the crystal would be $\sqrt[3]{N_0}$, where N_0 is Avogadro's number. Then the spacing ' a ' between the atoms in the crystal is given by,

$$a = \frac{\sqrt[3]{M/d}}{\sqrt[3]{N_0}} = \sqrt[3]{\frac{M}{N_0 d}}$$

If the substance is diamond, ($M = 12$, $d = 3.4$), the value of ' a ' = 1.8×10^{-8} cms.

In 1912, von Laue made the brilliant suggestion that if X-rays are actually

radiations of very small wave-lengths and if crystals are made of the orderly arrangements of atoms, the crystals must act as three-dimensional natural gratings

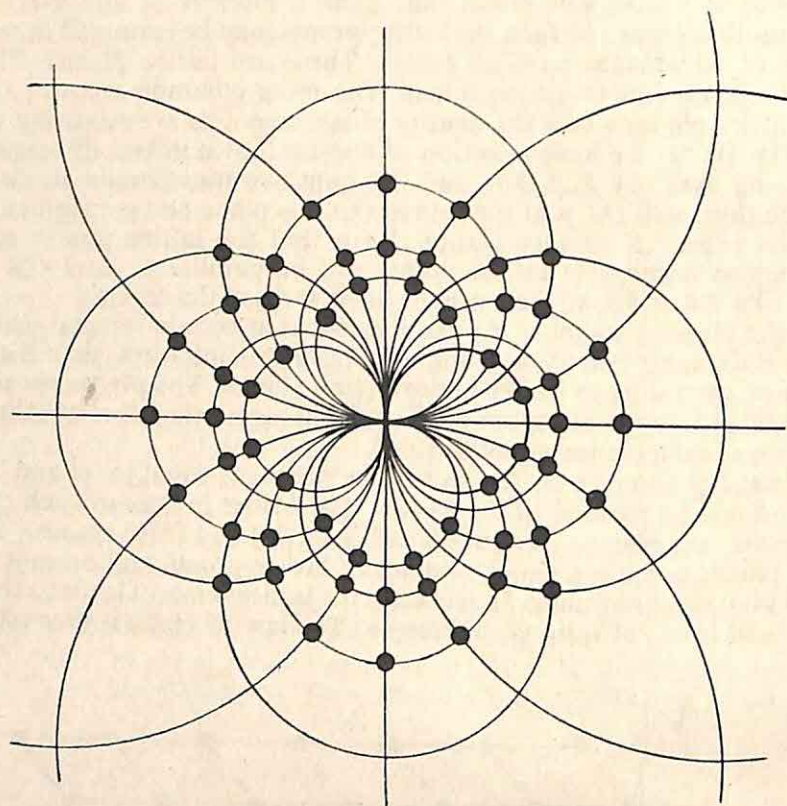


Fig. III.6 Theoretical diffraction pattern

for X-rays. Attempts therefore should be made to study the diffraction effects produced when X-rays are allowed to fall on a crystal. This would enable one to determine the wave-length of the X-rays.

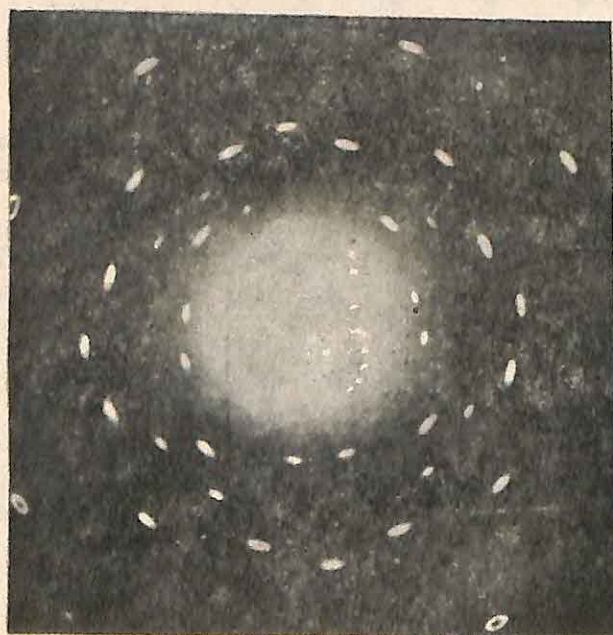


Fig. III.7 Laue diagram

Laue also showed theoretically that a beam of X-rays thrown upon a crystal would be partially converted upon transmission into a number of diffracted beams arranged symmetrically around the primary beam. If a photographic plate be placed directly behind the crystal, these beams would produce symmetrically arranged spots round the central image. Experiments were immediately performed by Friedrich and Knipping and the predictions of Laue were completely confirmed. Such photographs of diffracted beams are called 'Laue photographs.' In Fig. III.6 & III.7 are given the theoretical X-ray diffraction pattern and the Laue-photograph experimentally obtained for magnesium oxide.

This clearly demonstrated that X -rays are really waves of very short wavelength and also that there must be an ordered arrangement of atoms in the crystal. The full quantitative interpretation of the Laue diagrams proved very difficult at the time, particularly because of the use of white X -rays having continuous range of wave-lengths and the lack of knowledge of the exact arrangement of the atoms in the crystals. Soon however, W. H. and W. L. Bragg, father and son, developed a much simpler method which solved the problem. The original aim of the experiments was to use the crystals for studying X -rays. But it was soon the other way around, X -rays were employed to study the crystal structures.

III.5. The Bragg Method of Crystal Analysis. The space-lattice arrangement of atoms (or ions) in a crystal implies the existence of innumerable parallel planes containing the lattice-points or atoms. Each face of the crystal must have such lattice-planes parallel to itself. The Braggs showed that the scattering of X -rays by a crystal could be easily represented as 'reflections' from the planes of atoms parallel to a given face on which the X -rays are incident. They developed a very simple but useful relation between the wavelength of the X -rays and the spacing between the lattice-planes. The Braggs also found that the characteristic X -ray line spectrum could be isolated and the monochromatic beam of X -rays was used for crystallographic work.

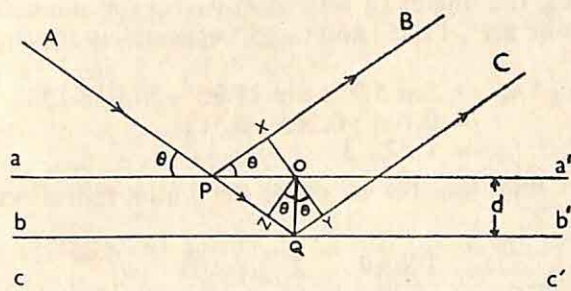


Fig. III.8 Reflection of X -rays from lattice-planes. (Bragg's law)

Consider a beam of monochromatic X -rays incident on a set of parallel and equidistant planes, called Bragg's planes, in the crystal structure. Let d cms be the distance between successive planes and let θ be the glancing angle, i.e., the angle between the direction of the incident beam and the planes. In Fig. III.8, the parallel lines (aa' , bb' , cc' , ...) represent the successive planes. Now consider an incident ray, say APQ , which meets two planes at P and Q . A portion of the ray AP will be reflected from P along PB , such that the angle BPa' will also be θ . Part of this ray will penetrate and will be reflected from inner planes bb' , cc' , ... The reflection of this ray from the second plane bb' occurs at Q in the direction QC , PB and QC being parallel. Draw the line QO perpendicular to the planes at Q meeting the first plane aa' at O . And also draw XOY perpendicular to PB and QC meeting them at X and Y ; XOY represents the wave front of the reflected beam.

The beams reflected from the parallel planes will generally combine in different phases and will destroy each other. Only under certain conditions of wavelength and angle of incidence, the reflected waves from different planes will combine in the same phase and reinforce each other. In this case it is evident that constructive interference will occur if the path PQY exceeds the path PX for waves scattered at P by an integral multiple of wavelength (λ). Draw OZ perpendicular to PQ and meeting the latter at Z . It is easy to see,

$$PX = PZ, \text{ and } \angle QOZ = \angle QOY = \theta.$$

Hence the excess path, ($PQY - PX$) is equal to

$$ZQY = 2QY = 2d \sin \theta.$$

This, for constructive interference, must equal $n\lambda$, i.e.,

$$n\lambda = 2d \sin \theta \quad \dots (III.1)$$

where n is an integer 1, 2, 3, ... etc. known as the order of reflection.

This is the famous *Bragg equation*, correlating the wavelength of the radiation with the spacing of the lattice-planes.

Now there will be innumerable planes even in a small thickness of the crystal (say more than a million planes per mm thickness). Practically complete interference occurs unless this condition with monochromatic radiation (eqn. III.1) is satisfied. As ' θ ' is changed, strong reflections flash out each time the equation holds with successive values of $n = 1, 2, 3, \dots$. At other intermediate values of θ , the intensity becomes negligible.

Two other points arise regarding this equation.

(a) Since the maximum limit of $\sin \theta$ is 1, it is evident that there is a lower limit to the spacing of the lattice planes to produce diffraction spectra for a given radiation. Say, for 1st order reflection (i.e., $n = 1$), we have

$$d = \frac{n\lambda}{2 \sin \theta_{\max}} = \frac{\lambda}{2}.$$

(b) For the different reflections from the same face of a crystal with a given monochromatic radiation (i.e., d and λ constant), we have

$$\sin \theta = \frac{n\lambda}{2d} = n \times \text{constant}.$$

That is, the sines of the angles of reflection of maximum intensities will bear a simple ratio. Thus, the angles of reflection (max) for the cube face of a NaCl-crystal are found to be 5.9° , 11.85° and 18.15° respectively for the successive orders. Then,

$$\begin{aligned} n_1 : n_2 : n_3 &= \sin 5.9^\circ : \sin 11.85^\circ : \sin 18.15^\circ \\ &= 0.103 : 0.205 : 0.312 \\ &\approx 1 : 2 : 3. \end{aligned}$$

Incidentally, we find, that for 1st order maximum reflection

$$d = \frac{\lambda}{2 \sin \theta} = \frac{\lambda}{2 \times 0.103} = 4.85 \lambda.$$

In other words, from the experimental determination of n and θ , we can express the lattice-spacing in terms of wave-length λ or vice versa. In fact, we have already seen, that with the knowledge of density and Avogadro number, we can calculate d and this enables the determination of λ . And once the wavelength of the radiation is definitely known, the same can be employed to find out the spacings of the atomic planes in other crystals.

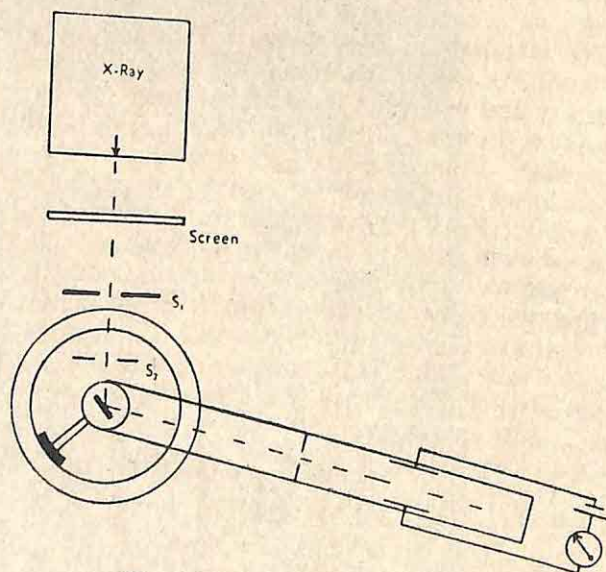


Fig. III.9 The Bragg-spectrometer

The apparatus used for the investigation of crystals is the Bragg spectrometer as shown in Fig. III.9. X-rays are generated by bombardment of a convenient

target and then suitably screened to obtain practically monochromatic radiations. Passing through S_1S_2 a sharp beam strikes the centre of a given face of a crystal. The crystal itself is placed just at the centre of a turn-table. Co-axially with the table and the crystal is a rotating arm carrying an ionisation chamber. Both the turn-table and the arm are provided with circular scales so that the angles through which they are turned can be directly obtained. The ionisation chamber is placed in such a way that the reflected rays from the face of the crystal directly pass into the chamber. The crystal table and the chamber are so adjusted that when the crystal rotates through any angle, the chamber will move through twice that angle. The ionisation chamber is filled with SO_2 -gas or methyl bromide vapour and the extent of ionisation is measured with the help of an electrometer connected with it. As the glancing angle (θ) is changed by turning the crystal face slowly, the strength of ionisation is recorded from the electrometer. These are plotted (θ vs I) and the maxima are obtained from the graph. The method was first successfully employed by the Braggs in the study of sodium and potassium chloride crystals.

III.6. The Crystal Structure of Sodium Chloride. In order to determine the crystal structure, we are really required to know the pattern of the regularly repeating spatial distribution of the constituents (atoms, ions, etc.). This is possible from the determination of spacings of some suitably chosen lattice planes of the crystals. For every crystal system, there are some three or four lattice-planes, whose spacings would reveal to us the position of the constituents. Sodium chloride is a cubic crystal, and for such crystals, it has been seen that the study of the spacings of (100), (110) and (111) planes would give us the required information. The relative positions of these planes in a cube can be seen from Fig. III.10, in which $ADEF$ is a 100-plane, $ADGC$ is a 101-plane and ABC is a 111-plane.

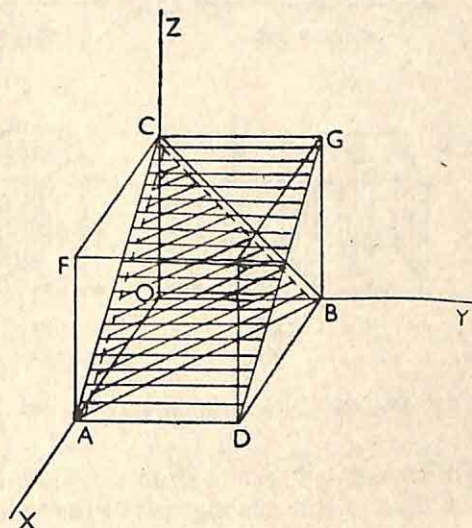


Fig. III.10 Lattice-planes of a cube

The space-lattice of cubic crystals may be of three types, simple cubic, body-centred cubic and face-centred cubic. In simple cubic lattice there is one structural constituent at each corner of the cubic cell. In the body-centred lattice there is one structural unit at each corner and also one unit at the centre of the cube. In the face-centred cubic lattice in addition to the structural unit at each corner, there is one unit at the middle of each of the six faces of the cube cell (Fig. III.11).

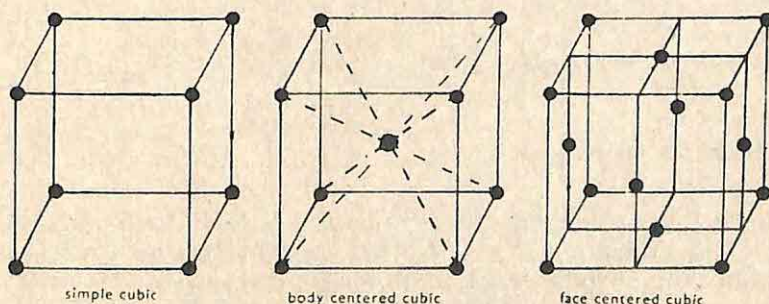


Fig. III.11 The types of cubic lattice

It is easy geometrically to calculate the spacings of the 100, 110 and 111-planes for all the three types of cubic lattices. The geometrical positions of the planes and the distances between them for all the three types are shown in Fig. III.12.

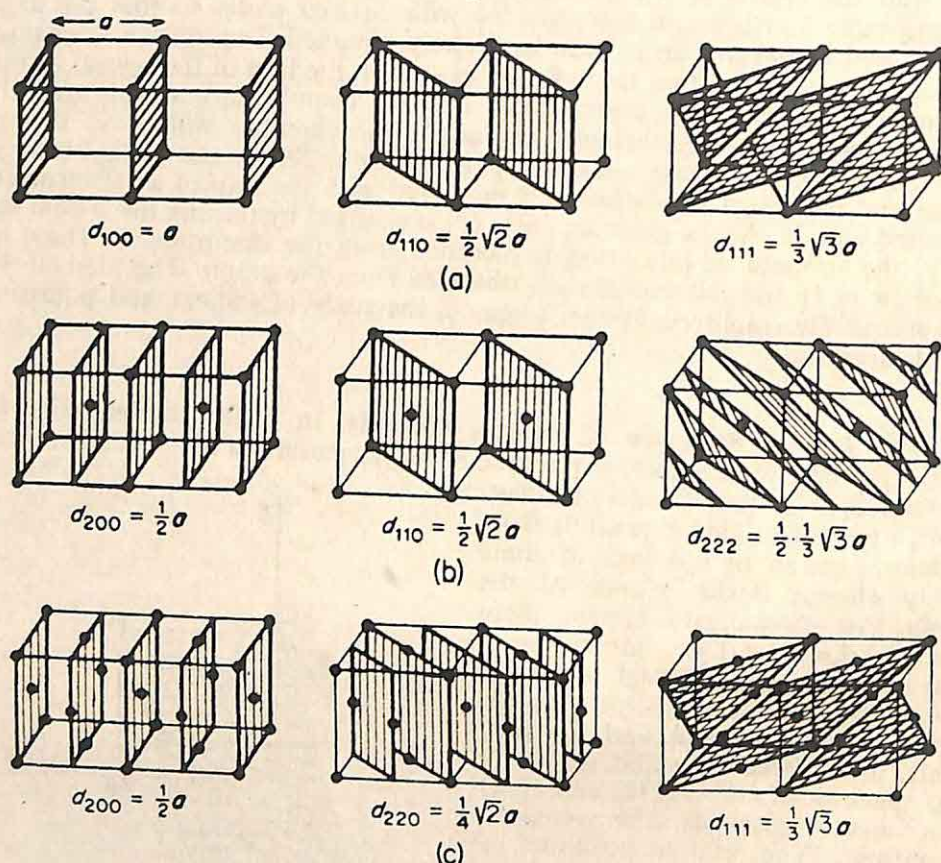


Fig. III.12 Spacings in cubic lattice : Simple, body-centred and face-centred cubic

The calculated results from these figures are shown in the Table below in terms of the ratio of the spacings (d) of the three types of lattice-planes, 100, 110 and 111.

TABLE : THE SPACINGS OF DIFFERENT LATTICE-PLANES
(a = side of the cube)

Lattice	d_{100}	d_{110}	d_{111}	
Simple cubic	a	$\frac{a}{\sqrt{2}}$	$\frac{a}{\sqrt{3}}$	$= 1 : 0.707 : 0.577$
Body-centred cubic	$\frac{a}{2}$	$\frac{a\sqrt{2}}{2}$	$\frac{a}{2\sqrt{3}}$	$= 1 : 1.414 : 0.577$
Face-centred cubic	$\frac{a}{2}$	$\frac{a}{2\sqrt{2}}$	$\frac{a}{\sqrt{3}}$	$= 1 : 0.707 : 1.154$

It is evident that experimental determination of the interplanar distance ratios will lead to the identification of the internal crystal structure. In fact, the Braggs examined the maximum reflections of monochromatic X-ray (k_α from Pd-antithode) beams from the NaCl-cube surface (100-planes) as also from planes at right-angle to the face-diagonal (110) and from planes perpendicular to cube-

diagonals. The intensities of reflections were plotted against the glancing angles of the beams as shown in Fig. III.13.

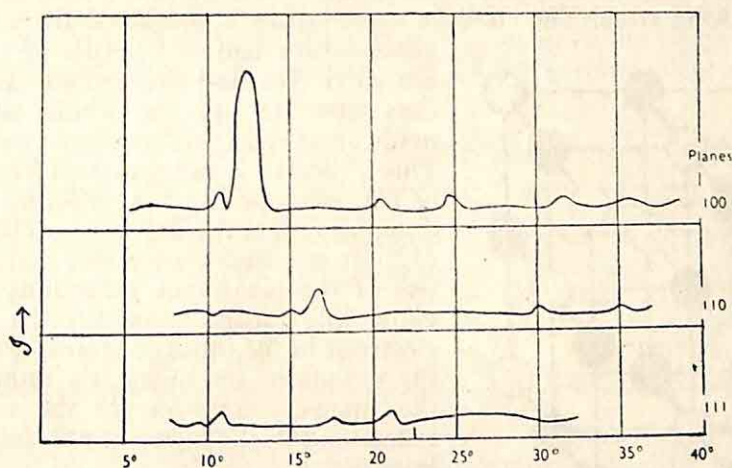


Fig. III.13 Intensity vs 2θ , (θ = glancing angle)

The angles at which maximum intensities of reflection for different orders were found for different lattice-planes are tabulated below.

TABLE : ANGLES FOR MAXIMUM INTENSITIES OF REFLECTION

	First order	Second order	Third order
Planes :	$n = 1$	$n = 2$	$n = 3$
(100)	5.9°	11.9°	18.2°
(110)	8.4°	17.0°	—
(111)	5.2°	10.5°	—

If we now consider only the 1st order reflections according to the Bragg-equation we have

$$\begin{aligned}
 d_{100} : d_{110} : d_{111} &= \frac{\lambda}{\sin 5.9^\circ} : \frac{\lambda}{\sin 8.4^\circ} : \frac{\lambda}{\sin 5.2^\circ} \\
 &= \frac{1}{0.103} : \frac{1}{0.146} : \frac{1}{0.091} \\
 &= 1 : 0.705 : 1.14.
 \end{aligned}$$

The same ratio is also obtained if the second order reflections are used. This ratio is the same as that theoretically predicted for face-centred cubic lattice. Sodium chloride crystal has therefore a face-centred cubic lattice.

Although the nature of the lattice in sodium chloride is established, the problem is not yet solved completely. We are also to ascertain the nature of the structural units. If the unit be the molecule, *i.e.*, Na-Cl ion-pair, there must be some distance between these two ions and the lattice-points should be the centre of gravity of the ion-pairs. This means that sodium and chloride ions will actually exist in two face-centred cubic lattices separated by some definite distance and obviously interpenetrating. On the other hand, if we place the chloride ions at the lattice-points, the neighbouring sodium ions must form another interpenetrating lattice. We have, therefore, to adjust two interpenetrating face-centred lattices. Exhaustive studies with such interpenetrating lattices have ultimately led to a structure as given in Fig. III.14.

This is really a face-centred cubic lattice of chloride ions into which a face-centred cubic lattice of sodium ions has interpenetrated. We are considering ions as structural units instead of atoms as there are now definite evidence of their existence in the solid state. The chlorine space-lattice is displaced from the sodium

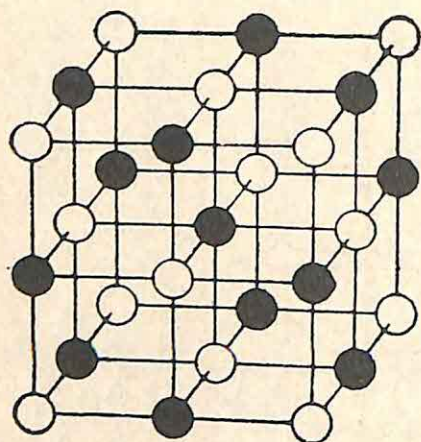


Fig. III.14 Face-centred cubic-lattice of NaCl

space lattice half the length of the edge of the cube. We find the sodium and chloride ions alternate and the whole cube is now made up of eight smaller simple cubic lattices. This structure is substantiated from the study of the intensities of the reflection maxima of different orders for the planes (100, 110 and 111). It is a well known fact that the intensities of the maximum reflections from any plane will depend upon (a) the number of electrons in the ions (or atoms) which scatter the radiation, the higher the number greater the intensity and on (b) the order of the reflection (n), the higher the order lesser the intensity.

In the structure given above, in 100 and 110 planes both chlorine and sodium ions occur, and hence the intensity will depend upon the order only. It is seen really that with increase in order the intensity of reflection maxima shows the usual decline for both these planes. (see table below). But in the case of 111-planes, there will be either chloride or sodium ions entirely. Planes containing sodium ions only are interposed halfway between planes containing only chloride ions. The effect of this interposition may be understood in the following way.

Suppose aa' , bb' are the 111-chlorine planes and ss' is the interposed 111-sodium plane, at a distance x from aa' (Fig. III.15). Suppose also that PQR and LMR are beams which after reflection are in phase, i.e., path difference is $n\lambda$. Now the path difference between PQ and AB (beam reflected from sodium plane) is $\frac{x}{d} n\lambda$.

Now after reflection ABQ will be in phase with PQR , if $\frac{x}{d} \cdot n\lambda$ is an integer. But we know $x = \frac{d}{2}$, hence $\frac{x}{d} \cdot n\lambda = \frac{n\lambda}{2}$. So when $n = 1, 3, 5$, etc. (odd number), the reflected beams will be in opposition. That is, for 1st order, 3rd order reflection

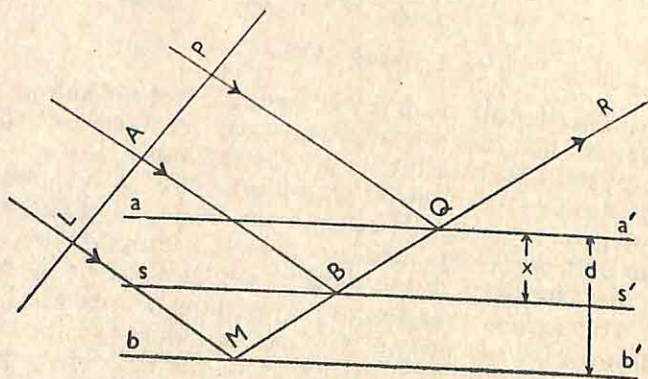


Fig. III.15

tions intensity will be less. It would indeed be zero if scattering powers of Na^+ and Cl^- were the same. But chloride ions being more powerful in diffracting rays,

some weak intensities will be available. But when $n = 2, 4$, etc., ($\frac{n\lambda}{2}$ is integral), the rays will be enforced after reflection and hence 2nd order, 4th order reflections will be quite strong. Exactly this is found experimentally and thus the proposed interpenetrating lattices in crystal structure are fully corroborated.

TABLE : RELATIVE INTENSITIES OF REFLECTION MAXIMA OF NaCl

Intensities for				
Planes	1st order	2nd order	3rd order	4th order
100	100.0	19.9	4.87	0.79
110	50.4	6.10	0.71	—
111	9.0	33.1	0.58	2.82

We may proceed further and find out the exact distance between the ions. The cube in Fig. III.14 is the unit crystal which repeats itself in every direction. The edge of this cube is the distance between two chloride ions or two sodium ions. Half of the edge will be the distance between a sodium ion and its neighbouring chloride ion. It is clear that every ion (say chloride) at the corner of the unit cube is shared equally by eight adjacent unit cubes. To each cube, we may allot $1/8$ of each of 8 corner chloride ions, i.e., $1/8 \times 8$ or 1 chloride ion. Besides, there are six chloride ions at face-centres, each of which is shared between two adjacent unit cubes or cells. Therefore, each unit cube has $\frac{1}{2} \times 6$ i.e., 3 more chloride ions. Total number of chloride ions per unit cell = 4. In this unit cell, there is one central sodium ion, and 12 others at the centres of edges, each of which is shared by four adjacent unit cubes. So, there are $1 + (12 \times \frac{1}{4}) = 4$ sodium ions possessed by each unit cell. Hence, every unit cell contains 4 sodium and 4 chloride ions, i.e., 4 sodium chloride molecules.

Now the molar volume of sodium chloride is M/d , where d is the density and M the mol. wt. Hence the volume of 4 molecules of NaCl is

$$v = \frac{M}{d} \cdot \frac{4}{N_0} \quad [N_0 = \text{Avogadro number}]$$

$$\text{or} \quad x^3 = \frac{M}{d} \cdot \frac{4}{N_0} \quad [x \text{ is the edge of the unit cell, which is a cube.}]$$

$$\text{or} \quad x = \left[\frac{M}{d} \cdot \frac{4}{N_0} \right]^{\frac{1}{3}} = \left[\frac{58.45}{2.17} \times \frac{4}{6.02 \times 10^{23}} \right]^{\frac{1}{3}} \\ = 5.63 \times 10^{-8} \text{ cms.}$$

$$\text{The interionic distance, } r_0 = \frac{1}{2}(5.63) \text{ \AA} = 2.815 \text{ \AA}$$

With the knowledge of the interplanar distance of lattice-planes for sodium chloride, we can determine the wave-length of the X-rays directed against it. In Bragg's experiment we have seen, for first order reflection ($n = 1$), the glancing angle θ is 5.9° (100-plane). Hence,

$$\lambda = \frac{2d \sin \theta}{n} = \frac{2 \times 2.815 \times 0.103}{1} = 0.58 \text{ \AA}$$

Now-a-days, beams of monochromatic radiation of known wave-lengths are obtained from definite anticathodes. These can be directly employed for analysis of unknown crystals.

Crystal structure of Potassium Chloride. Similar but interesting results are afforded from the study of potassium chloride. This is isomorphous with sodium chloride. Restricting to 1st order reflection from 100-planes with the same radia-

tions, the **glancing** angles for sodium and potassium chlorides are $\theta_{\text{KCl}} = 5.3^\circ$ and $\theta_{\text{NaCl}} = 5.9^\circ$. Then the ratio of the edges of the cube, assuming same face-centred cubic lattice for both, would be

$$\frac{d_{\text{KCl}}}{d_{\text{NaCl}}} = \frac{n\lambda}{\sin \theta_{\text{KCl}}} / \frac{n\lambda}{\sin \theta_{\text{NaCl}}} = \frac{\sin 5.9}{\sin 5.3} = 1.113$$

The molar volumes V_{KCl} and V_{NaCl} of the crystals are 37.46 and 27.94 c.c. respectively as determined from their densities. Hence, the ratio of the unit cube-edges of the two crystals, would be

$$\frac{d_{\text{KCl}}}{d_{\text{NaCl}}} = \left(\frac{V_{\text{KCl}}}{V_{\text{NaCl}}} \right)^{\frac{1}{3}} = \left(\frac{37.46}{27.94} \right)^{\frac{1}{3}} = 1.116$$

The identity justifies the assumption that potassium chloride crystal has the face-centred cubic structure.

But the first order spectrum from 100, 110 and 111-planes of potassium chloride shows that the spacings of these planes are in the ratio,

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$$

We have seen that such a ratio of spacings indicates the existence of a simple cubic lattice and not face-centred cubic lattice. A careful scrutiny will explain this apparently anomalous result obtained from diffraction studies. The ratio of 100 and 110-plane spacings are quite the same as expected. But 111-planes, which are composed of either all potassium ions or all chloride ions and are alternately present, do not give odd-numbered reflection maxima. The masses of potassium and chloride ions are nearly the same, and particularly the number of extra nuclear electrons is the same in both, hence the diffracting power of the 111 Cl^- -planes and 111 K^+ -planes are equal. In consequence when they are out of phase, the reflection maxima disappear. Alternatively, for diffraction purposes, a chloride ion and a potassium ion are equivalent, and as such, the face-centred unit cube is converted into smaller eight simple cubic lattices. It is immaterial whether a Cl^- or a K^+ ion is present at a lattice point. This is why spacing ratio obtained from spectrometer studies is that of a simple cube.

Excepting the halides of caesium, all the other alkali halides have interpenetrating face-centred cubic structures. Some metals like, Ag, Au, Cu etc., also have face-centred cubic structures.

III.7. Some Typical Crystal Structures. Face-centred cubic Lattice. We have already seen that sodium and potassium chlorides have f.c. interpenetrating cubic lattices. Similar arrangement is also observed in the crystals of oxides and sulphides of Mg, Ba, Sr, Ca etc. Quite a number of elements, such as solidified inert gases, also possess f.c. cubic structures as shown in Fig. III.14. The difference with NaCl crystal is that all the atoms are identical and the question of interpenetration does not arise. As before, from X-ray analysis the edge-length (a) of the unit cube can be easily determined. Each atom in such a cube has 12 equivalent neighbours. The distance between any two nearest atoms would be $a/\sqrt{2}$. Defining atomic radius as half the interatomic distance (i.e., assuming two atomic spheres are practically in contact in the structure) the radius of an atom = $\frac{a}{2\sqrt{2}}$. Below is appended a table showing the radii (r) of some atoms calculated by this method.

Element	'a' (Å)	'r' (Å)	Element	'a' (Å)	'r' (Å)
Ne	4.52	1.60	Cu	3.62	1.27
A	5.43	1.92	Ag	4.08	1.44
Kr	5.59	1.97	Au	4.07	1.44
I	3.83	1.30	Pt	3.92	1.36

On an average, each unit cube contains 4 atoms, ($1/8$ of each of 8 corner atoms, and $\frac{1}{2}$ of each of six face-centred atoms). The volume of 4 atoms, considered spherical, would be

$$4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi \left(\frac{a}{2\sqrt{2}} \right)^3 = \frac{\sqrt{2} \pi a^3}{6} = 0.74a^3$$

The volume of the unit cube is a^3 . Hence the extent of the space of the unit cube occupied by the molecules is $\frac{\sqrt{2} \pi}{6} (=0.74)$. That is, 74% of the space of the crystal is actually occupied by the molecules. This indeed is the closest packing possible in a cubic system.

III.8. Body-Centred Cubic Lattice. The alkali metals are examples of body-centred cubic lattice type, in which there are eight atoms at the corners of the cube and one at the centre (Fig. III.16). The closest distance between the atoms would be half the cube-diagonal, i.e., $\sqrt{3}a/2$, where ' a ' is the length of the edge of the cube. As in the previous section, the atomic radii may be taken as $\sqrt{3}a/4$. From measurements of angles at reflection maxima with X-rays, the values of ' a ' were determined. These are noted in the Table below.

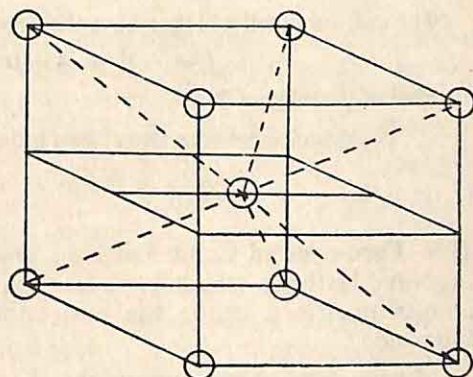


FIG. III.16 Body centred cubic lattice

In the case of crystals of elements all the atoms are the same. But there are compounds with body-centred lattices, in which the atom at the centre is different from that at the corner. Caesium chloride is such an illustration. In its unit cube, all the atoms at the corner are those of chlorine with an atom of caesium at the centre or vice versa. In fact it may be regarded as a case of two simple cube lattices (one of chlorine and one of caesium) interpenetrating.

In each unit of such body-centred lattice, there are two atoms present on an average ($\frac{1}{8} \times 8 + 1$). The space occupied by the two atoms is

$$2 \times \frac{4}{3} \pi r^3 = 2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}a}{4} \right)^3$$

Since the unit cube has a volume a^3 , the fraction of space actually occupied by the molecules is $\frac{\pi \sqrt{3}}{8} = 0.68$ or 68%. Evidently, the body-centred lattice is less economically packed compared to the face-centred lattice.

TABLE

Element	a (Å)	r (Å)	Element	a (Å)	r (Å)
Li	3.50	1.52	Cr	2.88	1.25
Na	4.30	1.86	V	3.04	1.32
K	5.20	2.25	W	3.16	1.37
Rb	5.62	2.42	α -Fe	2.87	1.24
Cs	6.05	2.62	β -Fe	2.91	1.26

Problem 1 : Calculate the density and atomic radius of elemental silver which crystallises in a face-centred cubic lattice with unit cell length of 4.086 Å.

(a) Simple face-centred cubic lattice contains four atoms. Hence density

$$\rho = \frac{4M}{v_m} = \frac{4 \times 107.88}{N_0 \times v} = \frac{4 \times 107.88}{6.02 \times 10^{23} \times (4.086 \times 10^{-8})^3} = 10.5 \text{ gms/c.c.}$$

$$(b) \text{ The length of face diagonal} = \sqrt{2a^2} = \sqrt{2 \times (4.086 \text{ \AA})^2} = 5.78 \text{ \AA}$$

$$\text{Hence interatomic distance} = \frac{1}{2}(5.78) \text{ \AA} = 2.89 \text{ \AA}$$

$$\therefore \text{ radius} = 1.45 \text{ \AA}$$

Problem 2 : Aluminium (density 2.69) crystallises with a f.c. cubic lattice. What is the distance of closest approach of Aluminium atoms in the crystal?

Since the crystal is a face-centred one, there are 4 atoms present per unit cell. Now, the volume occupied by 4 atoms is

$$v = 4 \frac{M}{N_0 \times d} = 4 \times \frac{26.98}{6.02 \times 10^{23} \times 2.69} = 64 \times 10^{-24} \text{ c.c.}$$

The unit cubic cell will then have the edge, l , given by

$$l = (v)^{\frac{1}{3}} = 4 \times 10^{-8} = 4 \text{ \AA}$$

Half of the edge = $2 \text{ \AA}$

$\therefore$ The distance between two closest atoms,

$$d = \sqrt{2^2 + 2^2} = \sqrt{8} = 2.83 \text{ \AA}$$

III.9. Face-centred Cubic Lattice : Diamond-structure Type. There are some other f.c. cubic lattices, which are some what complicated by the presence of atoms at definite positions inside the unit cube. The most important example is that of diamond.

From density measurements, the molar volume of diamond was found to be 3.42 c.c. The average atomic volume is then $\frac{3.42}{N_0} = 3.42/6.02 \times 10^{23} = 5.674 \times 10^{-24} \text{ c.c.}$

If the unit cube contains x atoms, then the volume of the unit cube would be $x \times 5.674 \times 10^{-24} = d^3$, where d is the length of the cube-edge.

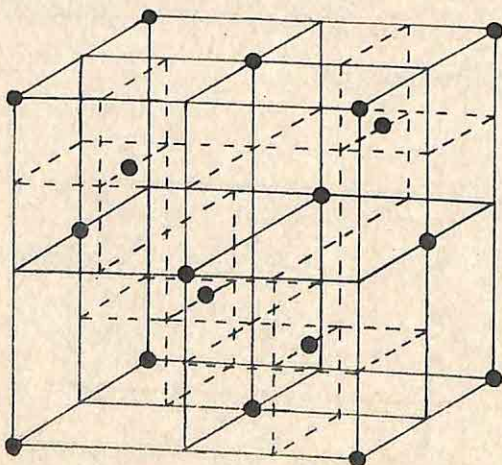


FIG. III.17 Unit cell of diamond crystal

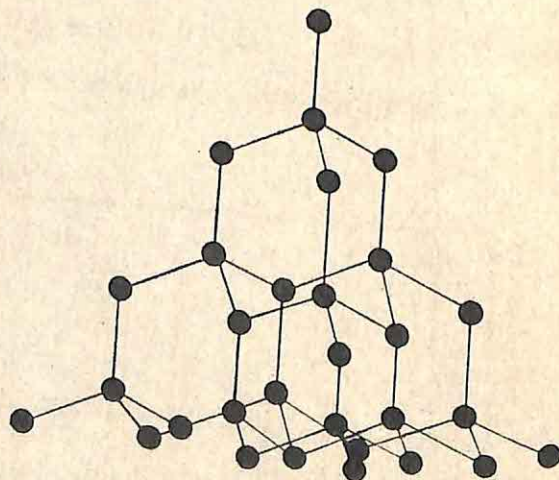


FIG. III.18 The tetrahedron structure of diamond

In a simple cube, $x = 1$; in a body-centred cube, $x = 2$, in a f.c. cube, $x = 4$ and so on. Putting different values of x , we have,

when $x = 1$,	$d = 1.784 \text{ \AA}$
$x = 2$,	$d = 2.248 \text{ \AA}$
$x = 4$,	$d = 2.831 \text{ \AA}$
$x = 8$	$d = 3.568 \text{ \AA}$ and so on.

Experimental observation of reflection from 100-planes showed that spacing of the lattice is $0.885 \text{ \AA}$. This means that simple cubic lattice ($x = 1$) is not present. The reflections from 111-plane on the other hand indicated their spacings as $2.05 \text{ \AA}$, so that length of the edge of the cube would be $2.05 \times \sqrt{3} = 3.55 \text{ \AA}$. This corresponds to the value $x = 8$. It may then be concluded there are eight atoms in the unit cube of diamond.

In a simple f.c. cubic lattice there are 4 atoms present. Four more additional atoms must then be accommodated in four new lattice points in the cubic lattice in such a symmetrical fashion that each has the same neighbourhood-relation. The only configuration satisfying this is to place one atom at the centres of each of the alternate small cubes as in Fig. III.17. We have thus eight atoms allotted to a unit cube on an average, retaining the symmetry.

Consider any one small cube containing an atom at the centre. The alternative corners are occupied by atoms. The central atom is equidistant from the corner. The distance is $\sqrt{3}d/4$. If all the neighbouring atoms are joined by such lines, the structure of diamond will be represented as in Fig. III.18. We have thus the picture of a regular-tetrahedron. Since d is $3.55 \text{ \AA}$, the carbon-carbon distance in diamond is $\sqrt{3}d/4 = 1.54 \text{ \AA}$. Though graphite has a different structure, several other elements of Group IV, such as Silicon, Germanium and grey Tin have the same crystalline configuration as that of diamond.

All the lattice sites of diamond crystal are filled up by carbon atoms. But in quite a number of binary compounds (e.g., ZnS) the central lattice-points of the alternate small cubes are occupied by different atoms. In zinc sulphide, if all the corner points and face-centres are occupied by zinc atoms, the centres of the four alternate cubes will be filled up by sulphur atoms. Each atom of one kind is symmetrically surrounded by four atoms of the other kind. The structure is like that of diamond (Fig. III.18). Cuprous halides, mercury sulphide, etc., have the same lattice structures. The cell-lengths of such structures are given in the Table below.

TABLE

Element	Cell-length $\text{\AA}$	Compound	Cell-length $\text{\AA}$
Diamond	3.56	ZnS	5.43
Silicon	5.42	HgS	5.84
Germanium	5.62	CuCl	5.41
Grey tin	6.46	CuBr	5.68

A large number of ternary compounds of AB_2 -type have face-centred cubic lattice structures, with centres of all the eight smaller cubes occupied by a different kind of atoms. In CaF_2 there are eight fluoride ions at the centre of small cubes, while the corner and face-centre lattice-sites are occupied by calcium ions. Each unit cell contains four calcium ions and eight fluoride ions, i.e., 4 molecules of calcium fluoride.

III.10. Hexagonal Close-packing Lattice. Assuming the atoms as spherical units, their most efficient packing is possible either in face-centred cubic or in hexagonal lattices. We have already seen what space the structural units occupy in a f.c. cubic lattice. Now we shall consider the hexagonal arrangement.

If identical round spheres or coins are arranged as closely as possible around each other in a plane, each unit in the arrangement will include six nearest neighbours (Fig. III.19). This arrangement of close packed spheres in a plane may be converted into a three dimensional one by adding layers above and below. Suppose a number of spheres are laid close together shown by hollow circles O (Fig. III.20). These spheres are really in contact though shown here as separate for clear understanding. A second layer of spheres, each marked by a $\oplus$ is now put over the first. These spheres of the second layer will nestle into the partial hollows created at the junctions of some of the triplets below. The $\oplus$ and the hollow circles O are not in the same plane.

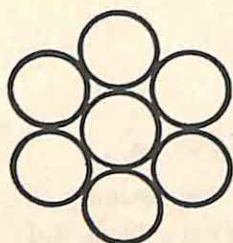


FIG. III.19

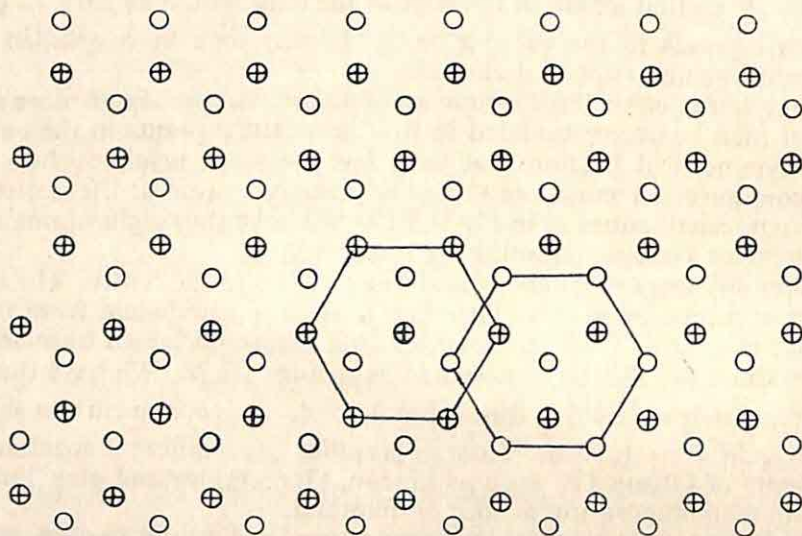


Fig. III.20(a) : 'O' represent atoms in 1st, 3rd, 5th layers while ' $\oplus$ ' represent atoms in 2nd, 4th, 6th layers in a close packing hexagonal structure, where two hexagonal structures are interpenetrating

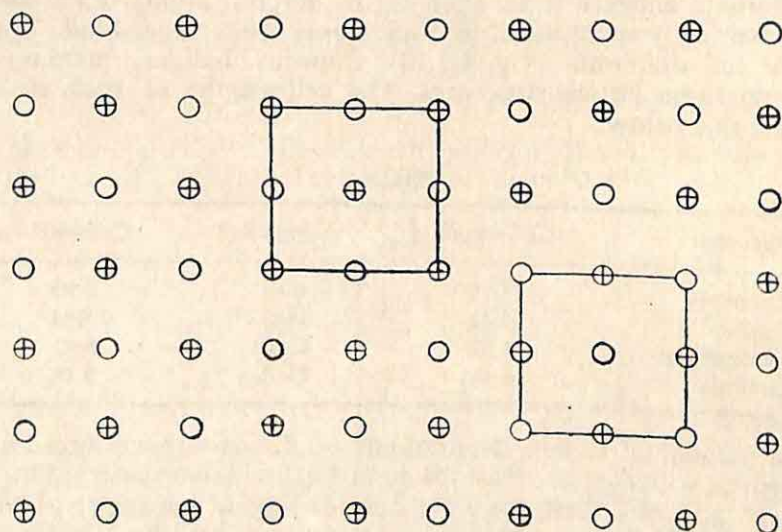


Fig. III.20(b) : 'O' represent atoms in 1st, 3rd, 5th layers while ' $\oplus$ ' represent the atoms in the 2nd, 4th, 6th layers in a face-centred cubic structure of an element. In a binary compound AB, in one layer A atoms occupy positions 'O' and B atoms occupy $\oplus$ positions. In the next layer, they interchange their positions. Thus two face-centred cubic structures become interpenetrating

The closed figure drawn by lines represent unit cells in the x - y planes in the respective cases.

A third layer can now be added over the second. Now a two-fold choice exists for arranging the third layer spheres. (i) The initial first layer may be repeated as in Fig. III.20(a) by placing every third layer sphere exactly overhead the corresponding first layer sphere. This gives rise to hexagonal packing, the layer being repeated as $ABABA...$ (Fig. III.21). (ii) Alternatively, the third layer spheres may occupy positions over the hollows of the first layer, which were not covered during formation of second layer. This gives rise to face-centred cubic close-packing, the layer being arranged as $ABCABCA...$ (Fig. III.21).

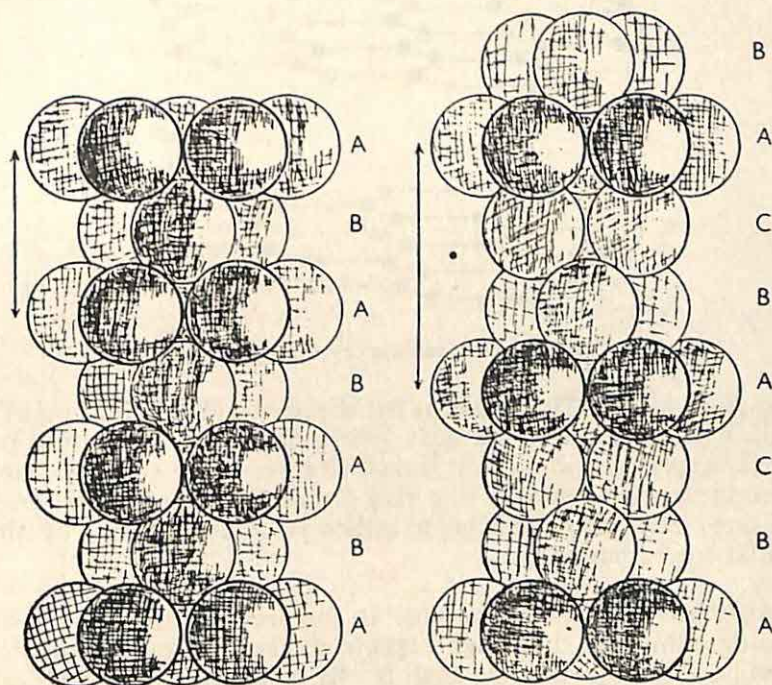


FIG. III.21 Close-packing

Most of the metals crystallise in f.c. cubic or in hexagonal lattice indicating that the metal atoms are spherical and close-packed. The hexagonal type is found in Be, Mg, Zn, Cd, Ti, Os, etc. The space occupied by the structural units in hexagonal cell close-packing can be geometrically evaluated and this is found to be about 74% of the total volume of the unit lattice.

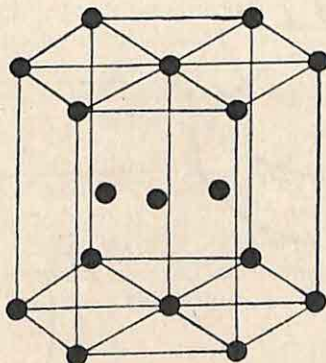


FIG. III.22 The hexagonal cell

III.11. Layer Lattices. There are a number of solids which consist of flat sheets of well-knit atoms. These sheets of atoms extend throughout the crystal in parallel layers. Though the forces between the neighbouring atoms in a layer are quite

large, but the forces between two layers are weak. Graphite (Fig. III.23) is the most outstanding example of such *layer lattice* crystals. Graphite belongs to hexagonal system and is really constituted of sheets of carbon atoms, the distance between parallel layers is about $3.41 \text{ \AA}$ which is relatively quite large compared to the carbon-carbon distance in each layer (which is $1.42 \text{ \AA}$). The parallel sheets are obvi-

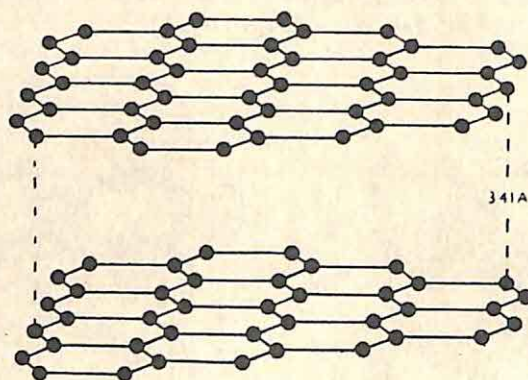


FIG. III.23 Graphite crystal lattice

ously held by weak forces. This explains the slippery and flaky nature of graphite. One layer can easily slide over the next giving rise to its lubricating properties. With each layer every carbon atom is linked to three other co-planar atoms symmetrically producing the benzene like ring-structures. Mica, black phosphorus, arsenic, antimony etc., also form layer lattice structures. Many of the silicate minerals exhibit similar structures.

III.12. Other Methods of Crystal Analysis. In the previous sections the outlines of the Laue photographic and the Bragg's spectrometric methods of studying crystal-line structures have been given. We shall briefly mention here two other methods widely employed now for crystal analysis.

(i) *The Powder Method.* This method was developed by Debye and Scherrer (1916) and by Hull (1917) independently. The sample of crystals in the form of a powder is taken in a thin-walled glass capillary tube. The experimental arrangement is shown in Fig. III.24. A beam of homogeneous X-rays fall on the powder,

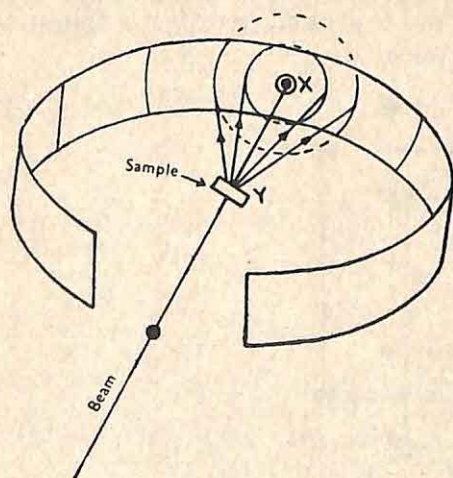


FIG. III.24 Powder-method

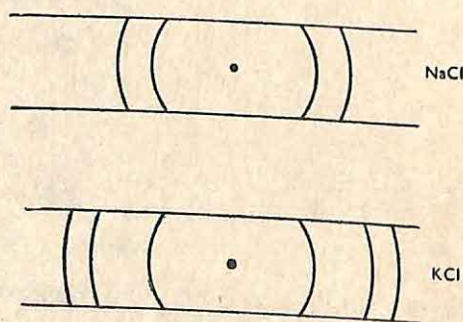


FIG. III.25 Powder-diffraction pattern

in which are present minute crystals oriented in all possible directions. Obviously there would always be a large number of crystals suitably oriented to produce maximum reflections say, from 100-planes. Since there would also exist different

orientations, for such crystals, parallel to a common axis, the diffracted beam will take the shape of a cone as shown in the figure. Similar such concentric cones will also be formed for other lattice-planes, say 110, 111, 220, etc. The diffraction-beam cones are allowed to impinge a circularly placed photographic film-strip. Each cone makes the image of two-arcs (or lines) at the positions where the cone cuts the film. The distance of the sample from the film (*i.e.*, XY , the radius) is known. Every symmetrical pair of lines in the film around the bright position at the centre of the incident undiffracted beam (Fig. III.25) corresponds to a particular lattice-plane of the crystal. The distances of these arcs from the incident beam-point X , is measured, and with the knowledge of the radius XY , the angle ' θ ' of maximum reflection is known. The calculation of spacings of the lattice planes thus becomes possible.

The powder diffraction patterns obtained from various solid substances are characteristic of the substances. For this reason, this powder X-ray diffraction is so often employed for qualitative and quantitative chemical analysis and to detect the presence of impurities. For quantitative estimation, the relative intensities of the lines with a standard diffraction film have to be measured. This diffraction photographic method sometimes enables us also to ascertain the composition of a mixture. Thus, in a mixture of potassium chloride and sodium bromide, the chemical analysis gives us the radicals only, but the diffraction photograph will confirm the compositions as well.

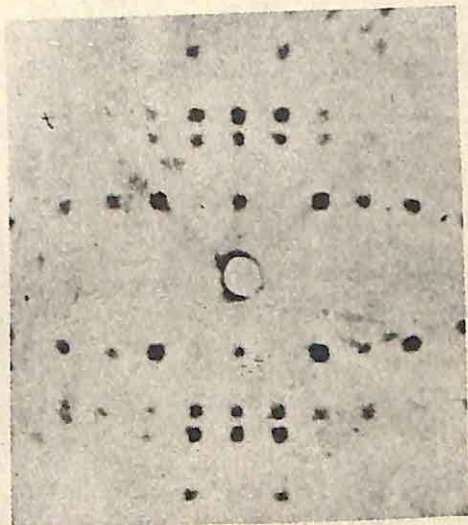


FIG. III.26 Rotation diffraction photograph

(ii) *Rotating crystal method.* Schiebold (1919) is responsible for developing this method. A minute well-formed crystal is placed in the path of a homogeneous X-ray beam with a suitable axis perpendicular to the beam. The photograph of the diffracted beam is taken on a film cylindrically placed around the crystal. The crystal is slowly rotated around the axis so that successive planes take up the orientation required for maximum reflection. Each such reflection produces a dark spot on the film. Different spots will correspond to different order of reflections. Photographs are repeated with the crystal rotating about all the three axes. The lattice-spacings and the size of the unit cell can be determined from the distance of the spots in the film, though interpretation is not always very easy (Fig. III.26). The method has been subsequently improved by oscillating the crystal only through a small angle (about 20°). A camera that moves the film back and forth along with the rotation of the crystal is employed. This makes it easier to identify the orientation of the crystal from the position of the spot.

III.13 Electron Diffraction. De Broglie's prediction (1924) that wave properties should also be associated with moving electrons was experimentally confirmed by Davisson and Germer in 1925 from their famous diffraction studies of electrons on a Nickel surface. An electron moving with a velocity v must also possess a wave property having a wave length λ , such that

$$mv = \frac{h}{\lambda} \quad \dots (a)$$

where m = mass of the electron = 9.1×10^{-28} gm.

and h = Planck's constant = 6.62×10^{-27} erg-sec.

If the electron passes across a potential difference of V , it acquires a kinetic energy ($\frac{1}{2}mv^2$) as a result of the acceleration acquired in the electric field. Hence

$$\frac{1}{2}mv^2 = Ve \quad (e = \text{electronic charge, } 4.8 \times 10^{-10} \text{ esu})$$

$$\text{or} \quad v = \sqrt{\frac{2Ve}{m}} \quad \dots (b)$$

$$\text{Hence,} \quad \lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}$$

Expressing V in volts, instead of e.s. units

$$\lambda = \frac{\sqrt{300} h}{\sqrt{2meV}} = \frac{12.2 \times 10^{-8}}{\sqrt{V}} \quad \dots (c)$$

In equation (c), putting,

$$V = 10 \text{ volts,} \quad \lambda = 3.8 \text{ \AA,}$$

$$\text{but when} \quad V = 40000 \text{ volts,} \quad \lambda = 0.06 \text{ \AA}$$

Hence, applying such a range of potential the electrons may be made to behave like X-ray waves. When an electron beam so accelerated is allowed to fall on a sample containing scattering centres, like crystal lattices, where the interatomic distances correspond, interference effects are observed. Thus, electron diffraction has become a new tool for investigation of solid structures. Since electronic beams are less penetrating than X-rays, electron beams are diffracted mostly from surface layers, which is an additional advantage. In fact, it is employed more for study of surfaces and surface films.

III.14. Crystal Forces. The forces operating in crystals to hold the particles together are classified as ionic bonding, covalent bonding, hydrogen bonding, metallic bonding and van der Waals' forces. It is true that in many cases two or three of these forces simultaneously operate though one of those would predominate.

(a) *Ionic Bonding.* In many crystals, like those of sodium chloride the structural units are ions and electrostatic forces predominantly operate between the ions. The forces really consist of the electrostatic attraction between ions of unlike charges and the repulsion-effect between the nuclei or inner shell of electrons of the two ions. The attractive and repulsive forces balance and give rise to a stable position with a minimum potential energy, when the interionic distance may be denoted by r_0 (say). This minimal potential energy distance is indeed the interionic distance in the crystal lattice. Now the decrease in energy in bringing the two ions from infinite distance to their positions in the crystal lattice measures their potential energy. Because the ions are at distance r_0 in the lattice the potential energy is minimum. The lattice energy of the crystal is opposite in sign but numerically equal to the minimum potential energy. An approximate evaluation of the lattice energy is possible in the following way, say for sodium chloride crystal. In this calculation, the effect of van der Waals' and other forces, which is really small is neglected.

The charges carried by sodium and chloride ions are ϵ_+ and ϵ_- and let the distance between them be denoted by r . Then the coulombic energy of attraction

$$\text{per unit cell} = \frac{-\epsilon^2 nA}{r} \text{ and the repulsive energy} = be^{-ar}$$

when A , a and b are constants, and n is the number of molecules of sodium chloride per unit cell. ' A ', called *Madelung constant*, depends on the lattice arrangement of ions and has been given definite values for each kind of lattice. The other constant ' a ' is usually taken as $3.3 \times 10^8 \text{ cm}^{-1}$ for all ionic molecules.

$$\text{Hence potential energy, } U = \frac{-nA\epsilon^2}{r} + be^{-ar} \quad \dots (1)$$

At equilibrium distance, r_0 ,

$$\frac{dU}{dr} = 0, \quad \text{hence} \quad \frac{nA\epsilon^2}{r_0^2} = abe^{-ar_0}$$

or
$$b = \frac{nA\epsilon^2}{ar_0^2 e^{-ar_0}}$$

Hence
$$U = \frac{-nA\epsilon^2}{r} + \frac{nA\epsilon^2 e^{-ar}}{ar_0^2 e^{-ar_0}} \approx -\frac{nA\epsilon^2}{r} + \frac{nA\epsilon^2}{ar_0^2}$$

Lattice energy per unit cell, changing the sign

$$-U = \phi = \frac{nA\epsilon^2}{r} - \frac{nA\epsilon^2}{ar_0^2} \approx \frac{nA\epsilon^2}{r_0} \left[1 - \frac{1}{ar_0} \right]$$

Lattice energy per gm-mole (ϕ_M) is

$$\phi_M = \frac{N_0}{n} \phi = \frac{AN_0\epsilon^2}{r_0} \left(1 - \frac{1}{ar_0} \right) \quad \dots (II)$$

where N_0 is Avogadro number.

From a knowledge of the lattice type (*i.e.*, f.c. cubic in the case of NaCl), r_0 can be obtained from the density of the crystal or from X-ray measurements. The lattice energy value is thus obtained. Indirect experimental support of the lattice-energy calculation is available from what is commonly known as Born-Haber cycle.

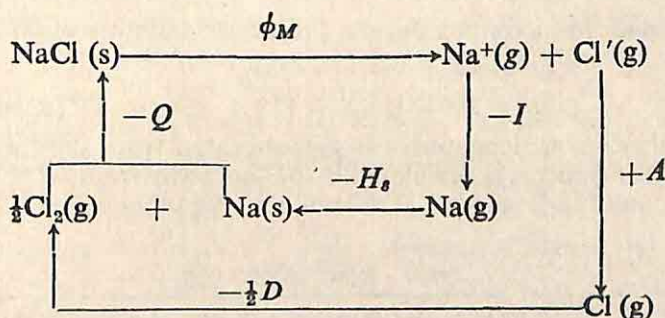
Problem : Calculate the lattice energy of NaCl (s). The Madelung constant is 1.748. The interionic distance from X-ray diffraction of the crystal is $2.82 \text{ \AA}$.

The lattice energy
$$\phi_M = \frac{AN_0\epsilon^2}{r_0} \left[1 - \frac{1}{ar_0} \right]$$

$$= \frac{1.748 \times 6 \times 10^{23} \times (4.8 \times 10^{-10})^2}{2.82 \times 10^{-8}} \left[1 - \frac{1}{3.3 \times 10^8 \times 2.82 \times 10^{-8}} \right]$$

$$\approx 7.6 \times 10^{11} \text{ ergs/mole} = 181 \text{ Kcals/mole.}$$

Born-Haber Cycle. For NaCl the cyclic process may be represented by the scheme,



where

- ϕ_M = lattice energy
- Q = heat of formation of NaCl
- H_s = heat of sublimation of Na
- D = heat of dissociation of Cl_2
- I = ionisation potential of Na
- A = electron affinity of chlorine.

The ionisation potential, I , is the energy absorbed in removing an electron from the atom, *i.e.*, $\text{Na} \rightarrow \text{Na}^+ + e$

The electron affinity ' A ' is the heat given out in the absorption of an electron in a process, *i.e.*, $\text{Cl} + e = \text{Cl}^-$

Starting with a gm-mole of NaCl crystal, the process consists of converting it into gaseous Na^+ and Cl^- ions and subsequently reuniting the ions to produce back the solid NaCl. The steps in the complete cycle are as follows :

Stages	Energy change (heat absorbed is positive, heat given out negative)
(a) One gm-mole NaCl is converted into $\text{Na}^+(\text{g})$ and $\text{Cl}^-(\text{g})$ ions $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$	ϕ_M
(b) An electron is taken out from Cl^- ion and the same is accepted by Na^+ ion $\text{Na}^+ + e \rightarrow \text{Na}$ $\text{Cl}^- - e \rightarrow \text{Cl}$	$-I$ A
(c) Chlorine atoms are converted into chlorine molecules, giving out heat of dissociation (D) $\text{Cl} \rightarrow \frac{1}{2}\text{Cl}_2$	$-\frac{1}{2}D$
(d) Sodium atoms are condensed to the solid state $\text{Na}(\text{g}) \rightarrow \text{Na}(\text{s})$	$-H_S$
(e) Chlorine is allowed to react with solid sodium atom producing the original substance $\text{Na}(\text{s}) + \frac{1}{2}\text{Cl}_2 \rightarrow \text{NaCl}$	$-Q$

The cycle is completed and the net energy-change must be nil. Therefore,

$$\phi_M - I + A - \frac{1}{2}D - H_S - Q = 0$$

or

$$\phi_M = Q + H_S + \frac{1}{2}D + I - A \quad \dots (III)$$

The quantities Q , H_S , D and I are directly experimentally measurable, but few independent electron affinity (A) values are known. That is why direct lattice energy values are not available from relation (III). On the other hand, the validity of this relation has been tested in an indirect way, by accepting the calculated value of lattice-energy (ϕ_M) from equation (II) and evaluating the electron affinity of chlorine.

From the data for sodium chloride, the electron affinity of chlorine is

$$\begin{aligned} A &= Q + H_S + \frac{1}{2}D + I - \phi_M \\ &= 98 + 26 + \frac{1}{2}(58) + 118 - 184 = 87 \text{ (Kcals)} \end{aligned}$$

That such evaluation is dependable is corroborated from the fact that when the electron affinity of chlorine is calculated in the same way from other alkali-chlorides, the values are found to be the same, as shown in the table below.

TABLE : BORN-HABER DATA

	Q	H_S	D	I	ϕ_M	$A \text{ (Kcals)}$
LiCl	97	39	58	124	201	88
NaCl	98	26	58	118	184	87
KCl	104	20	58	100	168	85
RbCl	105	19	58	96	162	87

The direct determination of electron affinity of chlorine from electron emission experiments also gave the value as 86 Kcals.

The electron affinities of other halogens Br, I and F have also been determined with the help of equation (III).

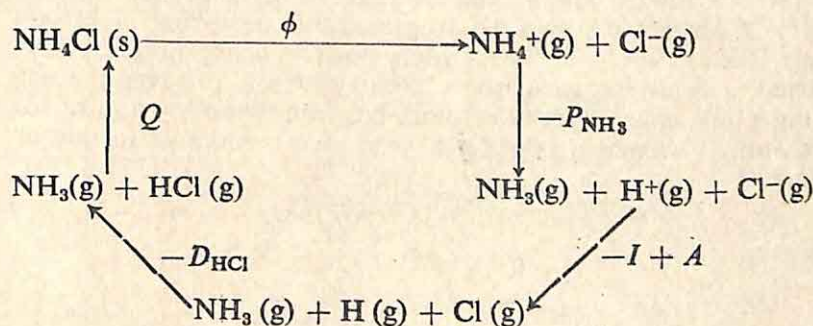
Moreover, the lattice-energy of other halides, like calcium fluoride, was calculated from Born-Haber cycle, using electron affinities of halogens derived

from alkali chlorides (just shown). These values corroborated with the lattice-energy calculated from ionic forces of crystals as in equation (II).

Crystals	Born-Haber	Calculated (electrostatic)
CaF ₂	689	697
MgF ₂	617	618

These evidences indicate that the procedure is sound. The forces in these crystals may therefore be adequately regarded as ionic forces.

One of the several interesting applications of Born-Haber cycle is the determination of the proton-affinities of water and of ammonia. The lattice-energy (ϕ) of ammonia has been determined carefully by Born-Haber cycle first. Subsequently, the following cyclic process is considered.



where P_{NH_3} = proton-affinity of ammonia
 Q = heat of reaction
 D_{HCl} = heat of formation of hydrogen chloride

Other symbols have the same significance as before.

Hence
$$\phi = P_{\text{NH}_3} + I - A + D_{\text{HCl}} - Q$$

Since all the quantities except P_{NH_3} is known, it can be easily evaluated.

Now, NH_4ClO_4 and H_3OClO_4 have been found to be isomorphous and have nearly identical X-ray maximum-intensity reflections, i.e., nearly identical lattice constants. It was assumed that their lattice energies are also the same, i.e., $\phi_{\text{NH}_4\text{ClO}_4} = \phi_{\text{H}_3\text{OClO}_4}$. Imagine now two cyclic processes separately performed with these two crystals as was done with NH_4Cl . Then,

$$\begin{aligned}
 \phi_{\text{NH}_4\text{ClO}_4} &= P_{\text{NH}_3} + I - A + D_{\text{HClO}_4} - Q_{\text{NH}_4\text{ClO}_4} \\
 \phi_{\text{H}_3\text{OClO}_4} &= P_{\text{H}_2\text{O}} + I - A + D_{\text{HClO}_4} - Q_{\text{H}_3\text{OClO}_4}
 \end{aligned}$$

Equating,
$$P_{\text{H}_2\text{O}} = P_{\text{NH}_3} + Q_{\text{H}_3\text{OClO}_4} - Q_{\text{NH}_4\text{ClO}_4}$$

The value of $P_{\text{H}_2\text{O}}$, i.e., proton-affinity of water, was found to be 182 calories/mole (Sherman, 1932).

(b) *Covalent bonding.* In many crystals, the atoms are the structural units and these are held together by covalent forces by pairing of electrons just as we find in carbon-carbon linkages of organic molecules. Diamond, Silicon, Germanium, Zinc Sulphide, Silver Iodide, Silicon Carbide are well known examples.

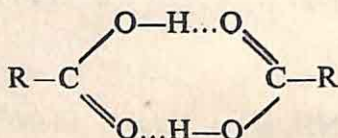
In diamond, there is a tetrahedral arrangement (Sec. III.9) and every carbon atom is covalently linked with four other equidistant atoms. There are really $2N_0$ carbon-carbon bonds in a gm-mole of diamond crystal. The heat of sublimation of diamond has been calculated from experimental results and found to be 170 Kcals/mole, i.e., bond-energy in diamond is 85 Kcals. The covalent C-C bond energy in hydrocarbons has also been found to be 80 Kcals showing a close resemblance in bonding in the two cases.

Similar three-dimensional covalent bonding in space lattice is also found in silicon carbide or silver iodide, or say, grey tin. All of them produce regular tetrahedrons. It is also not necessary that each atom should make contributions of same number of valence electrons.

Graphite represents an excellent example of two-dimensional display of covalent bonds. All the carbon atoms in any one plane are strongly covalently linked and behave like the C-atoms in anthracene, with the same interatomic distance of $1.34 \text{ \AA}$. The forces between the layers are however very weak and are of van der Waals' type.

In the case of selenium and tellurium, their valence shells are completed by sharing only two electrons of two adjacent atoms. In consequence, there are formed chains of atoms extending through the crystals. That is a case of one-dimensional covalent bonding (Fig. III.27). The individual chains are held together by much weaker forces. Similar cases we find in BeCl_2 or SiS_2 .

(c) *Hydrogen bonding.* Hydrogen atoms occurring in certain groups, such as $-\text{O}-\text{H}$ carry some positive charge and are thus attracted to electronegative atoms like oxygen and nitrogen thereby making a link, called hydrogen bond, between two oxygen or nitrogen atoms. A common example is seen in the dimer of formic or acetic acid.



This hydrogen bond is electrostatic in nature and is not very strong. The hydrogen bond energy is about 5 or 6 kcal.

The existence of such hydrogen-bonding in the crystal lattice is beyond dispute. The most discussed example is that of ice. In ice crystals we have a tetrahedral structure, each oxygen atom is surrounded by four hydrogen atoms at the corner of the tetrahedron. Two of these hydrogen atoms are covalently bound to the oxygen and other two form hydrogen-bonds. These latter two hydrogen atoms are covalently linked to a next oxygen atom. The distance between two oxygen atoms has been found to be $2.76 \text{ \AA}$, whereas the $-\text{O}-\text{H}$ bond-length is $1.00 \text{ \AA}$. That is, the hydrogen atoms in the crystal lattice are probably closer to one oxygen than the other.

Organic compounds such as phenols, carboxylic acids, etc., crystallise in a form supported by hydrogen-bonds. The specially situated hydrogen atoms link its own molecule to the oxygen or nitrogen of the next molecule. (See Chap. VI). The structure of protein crystal seems to be the result of hydrogen bonding.

(d) *Van der Waals' forces.* These forces are the same which we observed existing between molecules in a real gas leading to its non-ideality. The forces are really interatomic or intermolecular in the crystal lattice originating from dipole-dipole character and London dispersion forces. The forces are essentially weak and that is why organic crystals which are often held together, by such forces, are soft and low melting. We have already mentioned the existence of van der Waals' forces existing between lattice layers of graphite or mica, as also between the chains of selenium and tellurium. In the rhombohedral I_2 -crystal lattice, at each lattice point, a molecule of I_2 is held. It is thus a molecular crystal. Other molecular crystals are found in carbon dioxide, nitrogen, etc. Here also we find the units are primarily bonded through van der Waals' forces.

(e) *Metallic bonding.* The forces operating in the metal crystals are to a large extent different from those previously mentioned. The metals usually crystallise as body-centred cubic, face-centred cubic or close-packed hexagonal crystals; the latter two are most common. In both face-centred cubic and in close-packed hexagonal crystals, every atom has 12 surrounding neighbours, i.e., co-ordination number is twelve. In non-metallic elements, the atoms have never more than four immediate neighbours. In non-metals, therefore, the covalent bonding takes

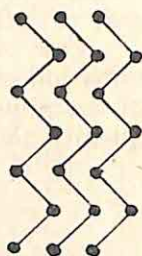


FIG. III.27
Lattice of
Selenium

place sharing four pairs of electrons at the most. In a metal, such pairing of electrons to form covalent bonds would need a very large number of electrons which are not available. In metals, the atoms are therefore linked by a special type of bond called "*metallic bond*." It is suggested that the atoms in a metal free some of their electrons and become positive ions. The matrix of positive ions remains embedded in a sea of mobile electrons. The free electrons really cement the positive metal ions. The conductance of the metals is due to the mobile electrons. The explanation of the position may be understood from what is now called the *Band theory*.

The electrons in an atom occupy some definite and sharp energy levels. The energy values of different levels are the same for all individual atoms. When the atoms take up definite positions in a crystal lattice, the electrons are subjected to a non-uniform electric field. In consequence, the energy levels are no longer sharp and are rendered into very closely spaced bands or groups of levels (Fig. III.28). The electrons may now occupy any position in the band. The bands are usually however separated by forbidden zones.

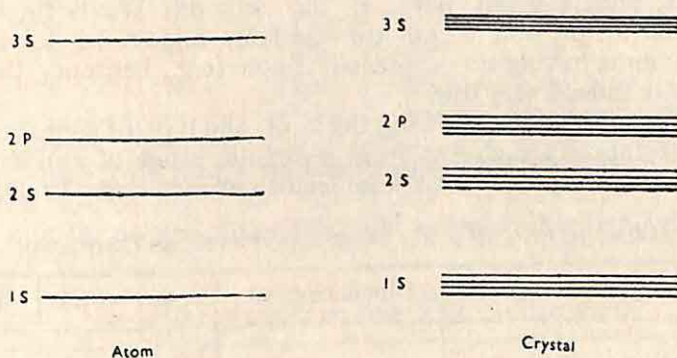


FIG. III.28 Energy levels in atoms and in crystals

The number of electrons available in the valence shells is not sufficient for pairing with all surrounding atoms to form covalent bonding. This means that, in metals, the lower bands are fully occupied but upper bands farthest from the nucleus are partially unfilled due to paucity of electrons. On the application of a potential, the lower band electrons will not move as all the levels in this band are filled up and Pauli principle forbids acceptance of additional electrons. But the electrons in the unfilled upper bands may shift to slightly higher level in the same band (Fig. III.29). There would then be a possibility of transfer of electrons from one atom to another, i.e., electrical conductance would occur. The valence electrons are delocalised and exchange freely between atoms. The atoms effectively become positive charges and the mobile electrons bind them together. The positive centres are held in positions oriented with respect to each other by exchange energy of electrons and this is responsible for cohesive forces in metals.

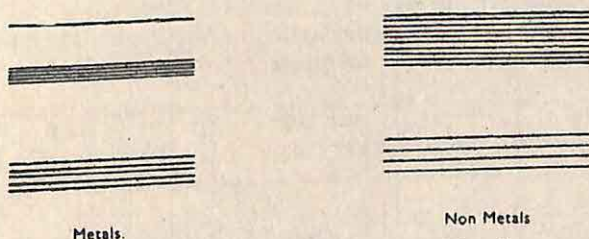


FIG. III.29 Energy levels in crystal bands

In non-metals, the position is different. Every atom being co-valently linked with the nearest surrounding atoms, the valence shell (octet) is saturated. All the bands of the crystal are completely filled. There is no unoccupied level in the uppermost band and the electron is unable to transfer itself even on the application of electrical potential. This explains the behaviour of non-metals as insulators.

The band theory has also been used to explain why some non-conductors under certain circumstances act as 'semiconductors'.

The cohesive forces and melting and boiling points. Due to the cohesive forces, an orientation or symmetry exists in the crystal and thereby the energy of the system is lowered. This gives a greater stability. Now, the greater the stability of the system, the greater is the amount of heat energy required to produce sufficiently powerful thermal agitations to break up the order and overcome the cohesive forces. Hence, the larger the cohesive forces between the atoms (molecules or ion) in a substance, the higher will be its melting point, and also the boiling point. Generally,

(i) When there are interionic or coulombic forces operating between the ions in the substance (e.g., NaCl), the melting or boiling points are high.

(ii) In metals, where the forces are again electrostatic in nature, the melting and boiling points are usually high.

(iii) When the cohesive forces are of the van der Waals type the interactions are weak, the melting and boiling points are much lower than those of the ionic compounds or metals. Even here, if the van der Waals forces be dipolar in character, the m. pt. and b. pt. are relatively higher. In non-metals and in covalent compounds having no permanent dipole (e.g., benzene), the melting and boiling points are indeed very low.

Below is appended a list showing the m.pt. and b.pt. of some compounds and metals. The substances are chosen from a definite range of mol.wt., so that the London forces operating between the molecules or atom may be comparable.

TABLE : M. PT. AND B. PT. OF DIFFERENT TYPES OF COMPOUNDS

Substance (mol. wt.)	Dipole moment	m. pt. (°C)	b. pt. (°C)
Ionic :			
Potassium chloride (74.5)	Very high	776	1500 (subl.)
Magnesium chloride (62)	"	1266	2239
Calcium oxide (56)	"	2580	2850
Metals :			
Iron (56)	metallic bonding	1535	3000
Nickel (59)	"	1455	2730
Copper (63.5)	"	1083	2395
Covalent :			
Benzene (78)	nil ($\mu = 0$)	5	80.4
Pentane (72)	"	-130	36
Butane (58)	"	-138	-0.5
Ethyl chloride (64.5)	Very low	-139	13
Diethyl ether (74)	"	-116	35
n-Propyl alcohol (60)	moderate	-127	97
Acetone (58)	moderate	-95	56
Acetic acid (60)	very high	16.6	118
Glycol (62)	Very high	-13	198
non-metals :			
Argon (40)	nil	-190	-186
Krypton (84)	"	-157	-153
Chlorine (71)	"	-103	-35

III.15. Atomic and Ionic Radii. It is necessary to record here a few lines about the radii of atoms and ions. These can be obtained from a study of the crystal structures.

For determination of atomic radii, we start with the crystal lattice of diamond. It has a regular tetrahedral covalent structure and it has been shown in Sec. III.9, that its interatomic distance is known from the determination of edge-length of the unit cell. Assuming that the atoms are spherical and are in contact, the radius of a carbon atom is taken as half the interatomic distance. The accepted value of the carbon-atom radius is $0.77 \text{ \AA}$ (for single bond covalent type). This is taken as the standard. The radius of another atom (X) is obtained by subtracting the carbon-radius from the interatomic distance of ' $C-X$ ' in the compound, say CX_4 -type covalent compound, determined with diffraction studies. In this way, the various atomic radii have been evaluated, some of which are given in the Table below. The values are true for single-bond covalent linking.

TABLE : ATOMIC RADII ($\text{\AA}$)

Atom	radius	Atom	radius	Atom	radius	Atom	radius
F	0.72	C	0.77	N	0.74	O	0.74
Cl	0.99	Si	1.17	P	1.10	S	1.04
Br	1.14	Ge	1.22	As	1.18	Se	1.14
I	1.33	Sn	1.40	Sb	1.36	Te	1.32

There is however some difficulty in determining the ionic radii. The interionic distances, obtained from lattice measurements, are taken as the sum of the radii of the two ions linked. But it has been found that the radius of an ion varies to some extent with the nature of the other ion to which it is bonded. This is evident from the following data.

TABLE : INTERIONIC DISTANCES ($\text{\AA}$) (F. C. CUBIC TYPE)

Cation	anion		Difference in radii of anions
	Chloride	Iodide	
Na^+	2.81	3.23	0.42
K^+	3.14	3.53	0.39

Difference in radii

of cations $K^+ - Na^+$

0.33

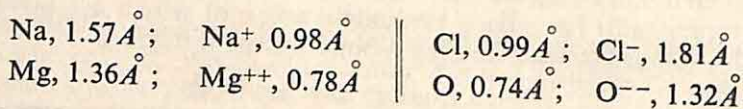
0.30

It is therefore necessary that the radius of some definite ion must be given a standard value. Wasastjerna, from the results of refractivity values, adopted $O^{--} = 1.32 \text{ \AA}$ and $F^- = 1.33 \text{ \AA}$ as the standard radii of the two ions. The radii of other ions can now be easily determined. For example, the interionic distance $Rb - F$ in rubidium fluoride crystal is $2.82 \text{ \AA}$. Hence the radius of $Rb^+ = 2.82 - 1.33 = 1.49 \text{ \AA}$. The value of the radii of some ions are given below. These values have been obtained from measurements of f.c. cubic type, i.e., NaCl-type lattice.

TABLE : IONIC RADII ($\text{\AA}$) (Co-ordination number, 6)

O^{--} (1.32)	F^- (1.33)	Ne (1.60)	Na^+ (0.98)	Mg^{++} (0.78)	Al^{+++} (0.57)	Si^{++++} (0.39)
S^{--} (1.74)	Cl^- (1.81)	Ar (1.91)	K^+ (1.33)	Ca^{++} (1.06)	Sc^{+++} (0.83)	Ti^{++++} (0.64)
Se^{--} (1.91)	Br^- (1.96)	Kr (2.01)	Rb^+ (1.49)	Sr^{++} (1.27)	Y^{+++} (1.06)	Zr^{++++} (0.87)
Te^{--} (2.11)	I^- (2.20)	Xe (2.20)	Cs^+ (1.69)	Ba^{++} (1.43)	La^{+++} (1.22)	Ce^{++++} (1.02)

It may be noted that the electronic structure is the same for all the elements in any row. But the radius diminishes with increase of resultant nuclear charge of cations. The radius of a cation is much smaller than that of an anion with equal charge. This is probably due to the shrinkage of the electron-orbits owing to the net positive charge at the nuclei. As expected, the ionic radii for both cations and anions increase regularly in any vertical column, *i.e.*, with atomic number in any group. On the other hand, a comparison of atomic and ionic radii will show that, for anions, the ionic radius is much larger than the atomic radius. For cations, it is reverse.



It is also found that the radii of ions play an important role in defining the form in which the substance would crystallise. Many of the AX -type compounds, where both the ions (A and X) have the same valence, crystallise in face-centred cubic form, as in sodium chloride. In this form, every ion is surrounded by six nearest oppositely charged ions. The number of units which surround a given unit in the crystal lattice as nearest neighbours is called its *co-ordination number*. That is, the co-ordination number in NaCl-crystal is *six*. In body-centred cubic lattice

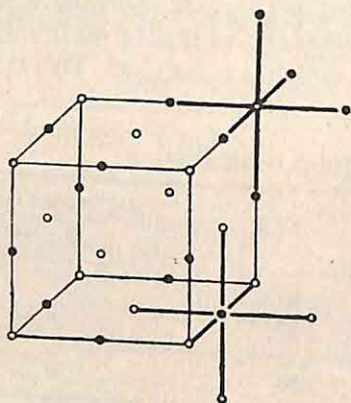


FIG. III.30(a) Face centred cubic lattice ;
6 : 6 Co-ordination, KCl type

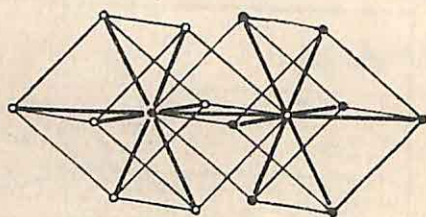


FIG. III.30(b) Body centred cubic lattice ;
8 : 8 Co-ordination, CsCl type

of caesium-chloride, the coordination number is *eight* (see diagrams) This co-ordination number depends on the size of the ions. The co-ordination number and therefore the lattice-form of the structure is decided by the number of larger ions (generally anions) which may be packed around a smaller ion (usually cation). The bigger the size of the cation, greater will be the number of oppositely charged anions to surround it and to remain in contact. The radius-ratio r_+/r_- therefore decides the co-ordination number. For example, in caesium chloride, eight Cl^- ions are at the corners of the regular cube with a Cs^+ at the centre. Each chlorine has a radius r_- and these touch each other. The length of the cube diagonal is $\sqrt{3} \cdot 2r_-$ (because edge-length is $2r_-$). The diameter of the hole in the centre is thus $\sqrt{3} \cdot 2r_- - 2r_- = (\sqrt{3} - 1)2r_-$. The cation which will fill this hole should have a

radius $(\sqrt{3} - 1)r_-$. The ratio of the ionic radii $r_+/r_- = \frac{r_- (\sqrt{3} - 1)}{r_-} = 0.73$. If

this ratio is less than 0.73, the co-ordination number cannot be eight and must be less. In this way ionic-radii ratio for different co-ordination numbers is obtained geometrically.

Co-ordination number $\rightarrow$

Ratio $r_+/r_- \rightarrow$

8
 >0.73

6
0.73-0.41

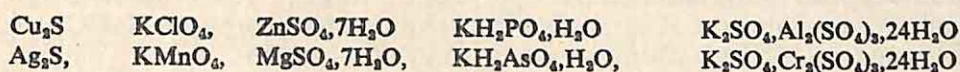
4
0.41-0.21

The ionic-radii ratio of some AX -type compounds are given below.

<i>CsCl-structure</i>	<i>NaCl-structure</i>		
CsCl = 0.93	KF = 0.98	KCl = 0.72	LiBr = 0.31
CsBr = 0.87	RbF = 0.92	NaF = 0.70	LiCl = 0.30
CsI = 0.78	RbCl = 0.82	KBr = 0.68	LiI = 0.28
	RbBr = 0.76	KI = 0.60	
	CsF = 0.82	NaCl = 0.53	
		NaBr = 0.49	
		NaI = 0.44	
		LiF = 0.44	

The radius-ratio thus indicates a general idea of the lattice-type of the crystal. The lithium halides retain NaCl-type lattice in spite of low radius-ratio-value because of the strong repulsion of the anions which are in close proximity. Similarly some of the fluorides such as RbF have NaCl-structure in spite of high r^+/r^- -values, due to low polarisability of the anions.

III.16. Isomorphism. For quite a long time many pairs of compounds of similar composition were known which would also crystallise in the same form and were said to be *isomorphous*. A set of common examples are :



A careful study of such isomorphous compounds led Mitscherlich to formulate the law of *isomorphism* which states,

"Substances possessing an equal number of atoms united in the same fashion exhibit identity of crystalline forms." It led to the concept that the crystalline form depends upon the number of atoms and the method in which they are united and is independent of their chemical nature. In other words, *substances having similar chemical character and crystalline form should have similar formulae*. We shall presently see that there are exceptions to this generalisation, but even then the principle is valid to a large extent and had been very useful in ascertaining correct atomic weights.

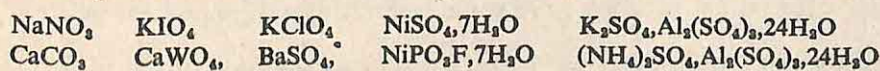
Mitscherlich found that the chemically similar potassium sulphate and potassium selenate are isomorphous. It was therefore assumed that the formula of potassium selenate would be K_2SeO_4 . On analysis it was found to contain 35.79% selenium.

$$\text{Hence} \quad \frac{x \times 100}{2 \times 39.1 + x + 4 \times 16} = 35.79$$

$$\text{or atomic wt. of selenium} \quad x = 79.2$$

Again Zirconium was formerly regarded as trivalent. But Potassium fluo-zirconate is found to be isomorphous with K_2SiF_6 and K_2SnF_6 . Hence, the fluo-zirconate should be K_2ZrF_6 i.e., zirconium like tin and silicon must be tetravalent.

It is evident that in isomorphous substances, the atoms substituted must be equal in numbers and should be of the same valence. This is borne out by the examples already cited. Instances are now known where isomorphous substances contain unequal number of atoms and also elements of different valence, e.g.,



In the last pair, the total number of atoms also differ. It has now been realised that the condition for isomorphism is the similarity of internal structure of the crystals rather than the similarity in chemical properties ; isomorphous substances must have geometrically similar units.

The identity of crystalline form is not the only criterion for isomorphism. It is true that isomorphous crystals have similar unit cells with almost same dimensions, e.g.,

	MgSO ₄ ·7H ₂ O	FeSO ₄ ·7H ₂ O	BaCO ₃	SrCO ₃
Interfacial angle	104°24'	104°15'	117°48'	117°18'
Axial ratio $a : b : c$	1.22 : 1 : 1.583	1.183 : 1 : 1.583	0.595 : 1 : 0.741	0.609 : 1 : 0.724

The converse is not necessarily true. Crystals with very similar crystalline constants have been found not to be isomorphous.

If a solution containing copper sulphate and ferrous sulphate be allowed to cool, crystals containing varying proportions of both of them are obtained. These are called *mixed crystals*, really solid solutions of the two. The isomorphous pure compounds are FeSO₄·5H₂O, and CuSO₄·5H₂O whereas the mixed crystals will have the composition (Fe_x, Cu_y) SO₄·5H₂O, such that $x + y = 1$. The formation of mixed crystals is a satisfactory criterion of isomorphism.

Again, if a small potash alum crystal be suspended in a saturated solution of its isomorph, say chrome alum, the size of the crystal increases due to the parallel deposit of the latter on the surface of the former. This is called *overgrowth*. Similarly, a calcite crystal suspended in a solution of isomorphous NaNO₃-solution will have the latter depositing on the crystal as overgrowth.

It is thus seen that isomorphism between two or more substances are to be determined from the following criteria: (i) similarity of crystalline form, (ii) formation of mixed crystals and (iii) formation of overgrowth.

From the detailed information of the structure of crystals, it appears that isomorphism is likely to occur when the following conditions are fulfilled: (1) the two substances must be of the same formula type, (2) the relative sizes of the constituent structural units must almost be the same, (3) the stereo-chemical form of the radical units, if any, must be similar, (4) the polarising properties of the structural units in the two substances should be almost equal. The crystals will then have same lattice type with almost equal axial ratios, resulting into equal molecular volumes. The substitution of one by another, or the formation of mixed crystals or overgrowths can then be easily understood. NaNO₃ and CaCO₃ (calcite) are both AB-type compounds and their molar volumes are NaNO₃ = 37.4 and CaCO₃ = 36.9. The sizes of the cations are almost equal, Na⁺ (0.95), Ca⁺⁺ (0.99). The anions NO₃⁻ and CO₃⁻ are both planar, with the three oxygen atoms at the corner of an equilateral triangle. Hence these two are isomorphous. But NaNO₃ is not isomorphous with KNO₃ for the cation K⁺ (1.33) is much larger and

hence the relative ion size ratio $\frac{r_+}{r_-}$ is different from that of NaNO₃.

In the same way, KMnO₄ and BaSO₄ are isomorphous because cations [K⁺ (1.33), Ba⁺⁺ = (1.35)] are equal in size, the anions MnO₄⁻ and SO₄⁻ are both stereochemically tetrahedral and similar; the axial ratios of the unit cells are also very nearly the same. On the other hand KNO₃ and KClO₃ are not isomorphous because ClO₃⁻ is pyramidal but NO₃⁻ is planar.

III.17. Heat Capacity of Solids. Another important property of solids is their heat-capacity, the study of which gave some interesting results.

1. Dulong and Petit's Law. In 1819, Dulong and Petit suggested from experimental data that "the atomic heat of all solid elements is a constant quantity and is approximately equal to 6.4 cal." Atomic heat is the product of the specific heat of the element and its atomic weight. Hence, specific heat $\times$ atomic wt. = 6.4 (approx.). The law holds for many solid elements as shown in Table A.

TABLE A (atomic heats)

Cu = 6.0	Sn = 6.4	Hg = 6.6
Ag = 6.2	Pb = 6.4	Cd = 6.1
Au = 6.2	Fe = 6.6	Zn = 6.0
Al = 5.8	Ni = 6.4	I = 6.6

Nevertheless, as given in Table B, the Dulong & Petit's Law fails completely in several cases.

TABLE B : (atomic heats)

Temp.	Diamond	Graphite	Silicon	Beryllium	Boron
10°C	1.35	1.92	4.6	3.4	3.32
200°C	3.2	3.4	5.6	4.9	—

The specific heats of solids are measured at constant pressure. The atomic heats given above refer to heat-capacities at constant pressure (C_P). The heat-capacity at constant volume (C_V) may be calculated from C_P -values with the help of a thermodynamic formula,

$$C_V = C_P - \frac{TV\alpha^2}{\beta}$$

where α = coefficient of thermal expansion, β = coefficient of compressibility.

Corrected thus, the Dulong & Petit atomic-heat constant should approach the value 5.9 cal instead of 6.4 cal.

Kopp's Law. Neumann, Joule & Woestyn made independent observations on the extension of Dulong & Petit's Law to compounds of similar chemical composition. Kopp (1865) made a systematic study in respect of molecular heats (mol. wt. $\times$ sp. heat) of compounds and made a generalisation; "*molecular heat of solid compounds is the sum of the atomic heat of the constituent atoms.*" This is known as Kopp's Law. Consequently, if there are n atoms present in a molecule the molecular heat will be *approximately* $6n$. The validity of this law is supported from the following experimental values.

TABLE (molecular heats)

CuO = 11.3	FeS = 12.0	AgCl = 13.1	BaCl ₂ = 18.8
HgO = 11.3	PbS = 12.2	KCl = 13.0	HgI ₂ = 19.1
NiO = 11.9	HgS = 11.9	CuCl = 13.6	PbI ₂ = 19.7

These laws had been quite useful in determining certain atomic weights. For example, Indium (eq. wt = 38) was found to have the sp. heat 0.057. Hence its approximate at. wt. = $6.5/0.057$ = 112. The true atomic weight is thus 3×38 = 114.

Again mercuric chloride (mol. wt. 271.5) had the sp. heat of 0.069. Then from Kopp's law, the molecular heat is 271.5×0.069 = 18.7, indicating 3 atoms in the molecule. The formula is then HgCl₂. The atomic weight of mercury is then 200.6, since the eq. wt. is 100.3.

A classical derivation of the law of Dulong & Petit had been proposed. In the crystal lattice, the atoms have only vibratory motion, the translational and rotational motions are absent. The vibration may occur in three directions and each mode of vibration has two degrees of freedom (Sec. I.31) each associated with energy, $\frac{1}{2}kT$. In a gm-atom there are N_0 atoms (Avogadro number) present. So the total energy of a gm-atom of solid is given by

$$E = N_0 \times 3 \times 2 \times \frac{1}{2}kT = 3RT. \quad \dots (III.2)$$

The heat-capacity at constant volume is the increase in E per degree rise in temperature. Hence, the heat-capacity (C_V)

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3R \approx 5.97 \text{ cal.} \quad \dots (III.3)$$

This is practically the value required by the Dulong & Petit Law. The classical theory however predicts that the atomic heat-capacity should be independent of

temperature. But in fact, there is observed considerable variation of the atomic heat with temperature particularly at the lower ranges of temperature. Dulong and Petit's Law fails at low temperature. In Fig. (III.31), the atomic heats of several solids are plotted against temperature, which clearly indicate the temperature-variation of the atomic heat. To explain these experimental findings, Einstein (1907) invoked the quantum theory.

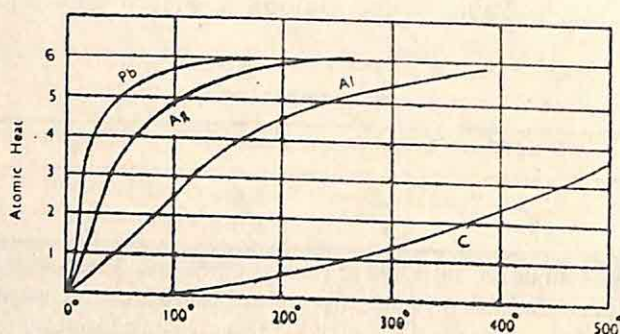


FIG. III.31 atomic heat of solids

2. Einstein's Equation of heat-capacity of solids. Einstein considered a solid (like copper) as an aggregate of atomic oscillators. Each of these oscillators is vibrating with a common mean frequency ν . In accordance with the quantum theory (Sec. V.16), the energy of an oscillator, vibrating with frequency ν in one direction is given by

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} \quad \dots (III.4)$$

[h , Planck Constant ; k , Boltzmann Constant]

Remembering the three possible directions of vibration and the total number N_0 (Avogadro number) atoms in a gm-atom, the total energy of a gm-atom of solid is

$$E = 3N_0 \frac{h\nu}{e^{h\nu/kT} - 1} \quad \dots (III.5)$$

The heat-capacity is then

$$\begin{aligned} C_V &= \left(\frac{\partial E}{\partial T} \right)_V = 3N_0 k \left(\frac{h\nu}{kT} \right)^2 \cdot \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \\ &= 3R \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \end{aligned}$$

This is Einstein's equation.

Putting $\frac{h\nu}{k} = \theta_\epsilon$, we have,

$$C_V = 3R \left(\frac{\theta_\epsilon}{T} \right)^2 \frac{e^{\theta_\epsilon/T}}{(e^{\theta_\epsilon/T} - 1)^2} \quad \dots (III.6)$$

i.e., C_V is a function of $\frac{\theta_\epsilon}{T}$, and may be written as $C_V = 3Rf(\theta_\epsilon/T)$ where θ_ϵ depends upon ν , which is a characteristic of the solid.

The Einstein equation gives temperature curves very similar to the experimental ones. Of course, the value of ν is determined from experimental results empirically. In fact, when temperature is high, that is, $h\nu/kT$ is quite small, we have, $C_V = 3R$. This is in agreement with the classical theory and the Dulong and Petit Law. Again, as T tends to zero, C_V also tends to zero, a conclusion in general agreement with experimental facts. But in the lower ranges of temperature, the calculated

values (from Einstein equation) fall more rapidly than do the experimental values. This disagreement is due to the neglect of the mutual interatomic forces. It was Debye (1912) who developed a modified equation which gave a very satisfactory agreement with experiment over the entire temperature range.

3. Debye's Equation. Debye suggested that (i) a solid is to be assumed as an elastic body, and the vibrations of the whole should be considered; (ii) the $3N_0$ -modes of vibration (in a gm-atom) of a monatomic solid are not all identical, as assumed by Einstein, but are distributed among a spectrum of frequencies. The frequencies range from zero ($\nu = 0$) to a maximum frequency ν_m , ($\nu = \nu_m$), which is a characteristic of the solid. Debye's ν_m is different from Einstein's ν and it can be shown that $\nu_m = \frac{4}{3}\nu$.

Now, it is known that if the total number of ways, z , in which an elastic medium of volume, V , can vibrate with a frequency, ν ; then dz between the frequency range $\nu + d\nu$ and ν will be given by

$$dz = \frac{4\pi V}{c^3} \cdot \nu^2 d\nu. \quad \dots (III.8)$$

If we take a gm-atom of the solid elements, containing N_0 atoms, the total number of vibrations possible will be $3N_0$. Remembering the frequency-range $\nu = 0$ to $\nu = \nu_m$, we have

$$\int_0^{\nu_m} dz = \int_0^{\nu_m} \frac{4\pi V}{c^3} \nu^2 d\nu = \frac{4\pi \nu_m^3}{3c^3} V = 3N_0. \quad \dots (III.9)$$

$$\text{Eliminating } V, \text{ we have, } dz = \frac{9N_0}{\nu_m^3} \nu^2 d\nu. \quad \dots (III.10)$$

We have seen the energy associated with each linear oscillator, $\bar{\epsilon}$ is given by

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT} - 1}.$$

The total energy of a gm-atom of solid will be, on substitution,

$$E = \int_0^{\nu_m} \bar{\epsilon} dz = \int_0^{\nu_m} \frac{h\nu}{e^{h\nu/kT} - 1} \cdot \frac{9N_0}{\nu_m^3} \cdot \nu^2 d\nu$$

$$\text{or } E = \frac{9N_0 h}{\nu_m^3} \int_0^{\nu_m} \frac{\nu^3}{e^{h\nu/kT} - 1} d\nu. \quad \dots (III.11)$$

$$\text{Putting } x = \frac{h\nu}{kT}, \quad \text{i.e., } \left[\nu^3 d\nu = \left(\frac{kT}{h} \right)^4 x^3 dx \right],$$

we have,

$$E = \frac{9N_0 (kT)^4}{(h\nu_m)^3} \int_0^{x_m} \frac{x^3 dx}{e^x - 1}. \quad \dots (III.12)$$

We can now consider the heat-capacity separately for high and for low temperatures.

(a) When temperature is high, x is small and therefore,

$$\int_0^{x_m} \frac{x^3 dx}{e^x - 1} = \frac{1}{3} x_m^3.$$

$$\text{Hence, } E = 9N_0 \frac{(kT)^4}{(h\nu_m)^3} \cdot \frac{1}{3} x_m^3 = 3N_0 kT = 3RT. \quad \dots (III.13)$$

The heat-capacity, $C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3R$.

That is, Debye's equation (III.11) conforms to classical requirement and to experimental values at higher temperatures.

(b) When the temperatures are low, x is large. The value of the integral reduces to $\pi^4/15$. That is,

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}.$$

Hence,
$$E = \frac{9N_0(kT)^4}{(h\nu_m)^3} \cdot \frac{\pi^4}{15} = \frac{3N_0}{5} \frac{(\pi kT)^4}{(h\nu_m)^3}$$

Differentiating,
$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{12\pi^4}{5} N_0 k \left(\frac{kT}{h\nu_m} \right)^3$$

or
$$C_V = \frac{12}{5} \pi^4 R \left(\frac{T}{\theta} \right)^3 = 464.6 \left(\frac{T}{\theta} \right)^3. \quad \dots (III.14)$$

where $\frac{h\nu_m}{k} = \theta$, called the *characteristic temperature* of the substance.

For a given substance, at very low temperatures,

$$C_V = \frac{464.6}{\theta^3} T^3 = aT^3. \quad \dots (III.15)$$

This is the well-known Debye's T^3 -Law. From equation (III.14), the value of θ and therefore, of ν_m of a substance for low temperatures can be calculated from an experimental value of C_V .* But with increase in temperature, T^3 -law fails and the value of θ does not remain constant. With proper adjustment Debye's equation agrees with experimental results both at low and high temperature ranges.

The Debye equation predicts that the heat-capacity of a solid is a function of temperature and depends upon only the characteristic maximum frequency, ν_m .

If the heat-capacities of different solids are plotted against $\frac{kT}{h\nu_m}$ (i.e., $\frac{T}{\theta}$) they should all fall on the same curve. Such a plot is shown in Fig. III.32. for a number

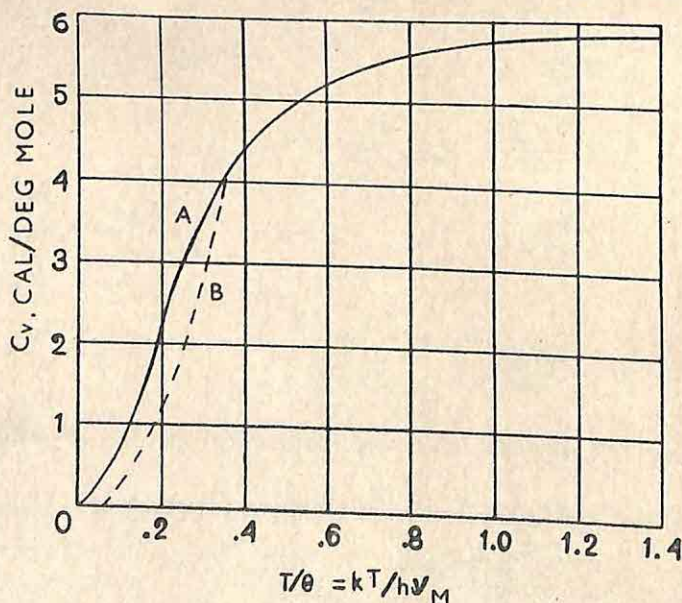


FIG. III.32

* ν_m can also be evaluated, if elastic constants are known, from the equation (III.9), where $\nu_m = (9N_0/4\pi Vc)^{1/3}$

of solids. The experimental results confirm Debye's formula very well. The values of the characteristic temperature θ of a few solids are given below.

DEBYE'S CHARACTERISTIC TEMPERATURES (θ)

Solid — θ	Solid — θ	Solid — θ
Na — 159	Zn — 235	C — 1910
K — 100	Hg — 96	Be — 1000
Cu — 313	Pb — 88	Fe — 433
Ag — 215	Mg — 290	Ni — 375
Au — 180	Ca — 230	Al — 389

REFERENCES FOR FURTHER READING :

- (i) Melting point and crystal structure,—Ubbelohde, *Qart. Rev.* 4, 356, (1950)
- (ii) 'Crystal chemistry' — Stilwell
- (iii) 'Crystal chemistry' — Evans
- (iv) Introduction to crystal analysis — W. H. Bragg
- (v) X-rays & crystal structure — W. H. Bragg & W. L. Bragg
- (vi) The structure of crystals — Wyckoff
- (vii) The nature of the chemical bond — Pauling
- (viii) X-ray crystallography — Buerger

Problems

1. Explain Weiss and Miller indices of a plane.
 - (a) What will be the Miller indices of a plane which makes intercepts of $\frac{1}{2}$, 2, and $3/2$ multiples of unit-distances on the three axes?
 - (b) If the Miller indices of a plane be 120, what are its Weiss indices?
 2. The first order reflection of a beam of X-rays from (100) plane of NaCl occurs at angle of $6^\circ 30'$, calculate the wavelength of X-rays. What would be the angle of reflection if X-rays of $\lambda = 1.54 \text{ \AA}$ be used?
 3. Sodium crystallises in a body-centred cubic lattice with a unit cube with side-length of $4.30 \text{ \AA}$. How many atoms of sodium are present in a unit lattice? What is the density of the metal?
 4. Sodium chloride, which has a face-centred cubic lattice, has a density of 2.17. What will be the spacing of the (100) planes? What is the edge-length of the unit cube?
- If the first order reflection of K_α -rays from palladium occurs at an angle of 5.9° from these planes, evaluate the wavelength of the X-rays used.
5. Aluminium crystallises in a face-centred cubic lattice and it has a density 2.70 gms/c.c. at 20°C . Calculate the distance between successive (100) planes. Estimate also Avogadro number.
 6. Nickel has face-centred cubic structure with $a_0 = 3.52 \text{ \AA}$. Calculate the distance apart of Ni-atoms lying in 100, 110 and 111 planes.
 7. Calculate the atomic heat of copper at 20°K using Debye's equation ($\theta = 314$).
 8. If the heat capacity per gm-atom of silver be $0.388 \text{ cal/}^\circ\text{K}$ at 20°C , what will be its heat-capacity at 1°K ?

THERMODYNAMICS

The study of a physical or a chemical process may be approached in two different ways. In the first place, the process may be treated in terms of atoms and molecules of the system, *i.e.*, on the basis of kinetic theory. On the other hand, the process may also be studied from a consideration of the energy changes involved. This is the thermodynamic approach. Thermodynamics, literally speaking, concerns itself with the flow of heat and it deals with relations between heat and work. The science of thermodynamics now governs not only the transformation of heat into work and *vice versa* but includes all kinds of interconversion of one kind of energy into another. It is based on three simple but empirically derived laws of nature acquired from long experience with energy. These laws can be subjected to rigorous mathematical treatment and they have yielded logical deductions correlating the various observable properties of matter. The relations predicted were tested experimentally for the last hundred years in different systems starting from the heat engines to the enzymatic processes in a living cell and were found to be rigidly valid.

Thermodynamics does not make any hypothesis as to the structure of matter. In contrast to the kinetic-molecular theory, it derives, from the basic laws, relations between properties experimentally observed but does not offer any explanation as to why these properties arise in a system. The approach in thermodynamics is thus entirely different from that in the atomic constitution of matter. For example, in kinetic theory we consider the pressure of a gas as a measure of the impact of the molecules on the wall per second, while in thermodynamics, pressure is a property of the state of a system, regardless of its inherent constitution, based on the observation of the body as a whole. Likewise, temperature is, according to kinetic theory, a measure of the average kinetic energy of the molecules while it is a simple property of state from the view-point of thermodynamics.

Before we begin with the laws of thermodynamics it is necessary to define some of the terms most commonly used in thermodynamic discussions.

IV.1. Heat, Work and Energy. If an object, say a table, is pushed by the hand, it may be displaced from its original position. We consider this as a mechanical work (or simply, work) done by muscular effort. In fact, whenever the application of a force causes a displacement of a system, mechanical work is done. The magnitude of the work is measured by the product of the force and the displacement caused. Thus, work

$$W = F \times \Delta l$$

where F is the force and Δl is the displacement caused. The lifting of a weight, the expansion of a gas by moving out a piston, the winding or unwinding of a spring, the turning of the blades of a wheel, are common instances of such mechanical work. The performance of the work need not necessarily be always achieved by muscular effort. The work may be produced in diverse ways. If a quantity of electricity Q is transported along a wire under an electromotive force E , then we consider this as electrical work, $W = E \times Q$.

The usual convention in thermodynamics is that the work done by a system is positive, whereas the work done on the system is negative. To be more precise in the concept of work, it would be convenient to recall here a few relevant facts of experience.

Heat generated by the burning of coal ultimately enables the steam-engine to pull the train, *i.e.*, to perform work. Conversely, the mechanical work spent in rubbing two blocks of ice or in the boring of a cannon generates large

quantities of heat. There is thus an intimate relation between heat and work, one can yield the other. We need not at the moment enter into the quantitative relation between the two.

An object A placed at a certain height and tied to a weight over a pulley would lift the latter when the object A descends to the surface of the earth. We state that the body A at the higher level possesses potential energy at the cost of which the work of lifting the weight is being performed (Fig. IV.1).

Electricity passed through a circuit may be made to produce the rotation of the armature of a motor used for lifting a weight or winding a spring. Conversely, the work done in turning the blades of a turbine would generate electricity. This is an instance of the conversion of electrical energy into work and *vice versa*. On the other hand, electricity led through a resistance would produce heat.

In a chemical reaction, say between zinc and copper sulphate, large amounts of heat are produced. The same chemical change carried out in a voltaic (Daniell) cell would provide electrical energy instead of heat. Here the chemical energy is being converted into heat or electrical energy. Numerous such illustrations may be cited.

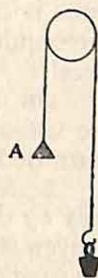


FIG. IV.1

Broadly speaking, two facts emerge out of these. Firstly, the different systems possess something (really the energy) which can yield work ; and secondly, all these different kinds of energy are interconvertible. Energy should therefore be defined as a property which can be transformed into or produced from work.

In the various natural phenomena, energy manifests itself in different forms, such as, mechanical, internal, chemical, radiant, electromagnetic, surface energy etc. From this definition of energy, work itself becomes equivalent to energy and is an observable manifestation. In fact, different forms of energy are expressed in terms of work.

Heat, obviously, is another form of energy since it can yield work or can be produced from work. But heat is somewhat different from other forms of energy such as electrical or chemical. All other forms of energy can be completely transformed into work, but heat cannot be wholly converted into work. Any attempt to convert the whole of a quantity of heat would affect a permanent change in the system or the neighbouring systems. There is another aspect of heat which requires attention. When two objects with different temperatures come together, one with the higher temperature loses heat energy and the other gains it. That is, energy in the form of heat flows from a higher to a lower temperature. Hence, heat is energy *in transit*. Only during the process of flow we are conscious of this form of energy. But when the flow ceases, we do not speak about the heat present in a body. "Heat in a body" is meaningless. What may be present in a body is the energy. This energy, by out-flow of heat, would be decreased and would be increased by in-flow of heat. Likewise, it would be incorrect to speak about 'work in a system'. The system during a physical or chemical change may yield work at the expense of energy.

IV.2. Thermodynamic Systems. For the purpose of thermodynamic considerations, a *system* is defined as any material or quantity of matter, chosen separately from the rest of the universe, enclosed by boundary surface. The boundaries of the system may be real or imaginary, but the existence of the boundaries is of importance in order to visualise the system distinctly from the rest of the universe. A quantity of a gas in a closed cylinder has real and defined boundaries, but when the same gas flows through a zigzag pipe, its boundaries constantly change and have to be followed in imagination as it progresses. Any other material or body, near or distant, besides the system chosen, *i.e.*, the rest of the universe is spoken of as the *surroundings*. It is however not necessary that the systems should have any definite shape or volume. A thermodynamic system may contain one or more kinds of matter and may be homogeneous or heterogeneous in character.

The boundary walls of a system may be of two types. The walls may allow the transmission of heat through them, into or out of the system. Such walls are *diathermal* walls. On the other hand, a system may be enclosed by boundary walls

which would not permit any heat to enter into the system or to come out of the system. These walls are termed *adiabatic* walls. A liquid contained in a glass beaker may be easily heated by a Bunsen burner, the glass walls behaving as diathermal boundaries. If the liquid is kept in a silver-mirrored double-walled Dewar vessel, heat from a burner can little affect the temperature of the liquid within. The boundary walls here are adiabatic. A system wholly enclosed by adiabatic walls is called an *isolated system* and is incapable of exchanging energy with its surroundings. There is also no possibility of transfer of matter across the boundaries.

On the other hand, *closed systems* are those in which energy-exchange with the surroundings is possible but transfer of matter across the boundaries is not permitted. There may be internal change in composition.

State of a System. The thermodynamic state of a system can be expressed only by describing the characteristics possessed by the system. A system to be in a given state must have definite values assigned to its properties. Various properties such as composition, volume, pressure, temperature, refractive index, viscosity, dielectric constant etc., are associated with a system. Of these, only the first four, namely, composition, volume, pressure and temperature are of fundamental importance and are called thermodynamic properties or parameters.

These four variables of the system are generally sufficient to completely define a system thermodynamically. These parameters or co-ordinates of the system are directly experimentally measurable and do not require any assumption regarding the structure of the matter. It is, of course, obvious that if the system contains a homogeneous matter, the composition is automatically fixed. The pressure, volume and temperature of a system are interrelated with one another in the form of equations of state. Exact quantitative relations between these three parameters of a system are not known for solid, liquid or heterogeneous system. In the case of ideal gases ($PV = RT$) or in the case of systems containing real gases, more or less accurate relations (say, van der Waals') are well-known and can be experimentally established. In such cases, if any two of these variables be specified, the third is fixed. Thus, if pressure and temperature of a system either homogeneous or of known mass and composition be known, the volume would have a fixed value. Hence it is said that the thermodynamic state of a simple homogeneous system is defined by specifying any two of the three variables.

IV.3. Equilibrium. We know that the state of a system is determined by the variables of the system, like pressure, temperature etc. If the variables are found to change in a given system, then the system must also be changing in its state. Such a system evidently is in an unstable condition.

In a system left to itself, the parameters have a tendency to be uniform throughout the system. The pressure and temperature thus become uniform at all points of the system.* If different parts of the system have different pressures or temperatures, the parameters cannot be specified and the thermodynamic state of the system cannot be defined. When complete uniformity in the magnitudes of the variables is acquired, a steady condition is set and the system is said to have attained *equilibrium*. For attainment of complete equilibrium, there should be mechanical, thermal and chemical stability.

When there is no unbalanced force existing between different parts of the system or between the system and the surroundings, the system is in *mechanical equilibrium*.

If the temperature at all parts of the system be the same and identical with that of the surroundings, the system is in *thermal equilibrium*.

When the composition of the system remains fixed and definite, the system is said to be in *chemical equilibrium*.

The mechanical equilibrium therefore refers to uniformity of pressure, the thermal equilibrium to uniformity of temperature and the chemical equilibrium to the constancy of chemical composition. Even after attainment of mechanical and thermal equilibria, a system may permit chemical changes to continue. At

*In a heterogeneous system, this would apply to each homogeneous part of the system.

the same temperature and pressure, a mixture of hydrogen and iodine may continue to react slowly for days, until chemical equilibrium is reached. Similarly, a system may be in chemical and mechanical equilibria, without being in thermal equilibrium.

A system which satisfies all the three equilibria is said to be in *thermodynamic equilibrium*. Its composition and properties would undergo no observable change. When a system is in thermodynamic equilibrium, its properties have definite magnitudes. Whenever the system comes to that particular state of thermodynamic equilibrium, its properties will have the same magnitudes, regardless of what might have occurred to the system previously.

IV.4. Internal Energy. Energy may occur in different forms such as mechanical, electrical, chemical, internal and others. The nature of the forms like electrical, mechanical etc. are more or less easily conceived, but the concept of the 'internal energy' is not so obvious. A thermodynamic system, containing some quantity of matter, in virtue of its very existence, must possess a store of energy. This is sustained by the common observations in diverse isolated systems; e.g., (a) a liquid freezes into a solid yielding heat energy, (b) zinc & copper sulphate (in Daniell cell) react producing electrical energy, (c) steam expands from higher to lower pressure yielding mechanical work, (d) carbon monoxide and oxygen unite producing heat. Unless the systems had inherent energy within how could they, isolated from the surroundings, yield work or other forms of energy by themselves. We are thus led to believe that every system has within itself a definite quantity of energy called the *internal energy* or *intrinsic energy*. The amount of the internal energy depends on the thermodynamic state, i.e., the thermodynamic parameters of the system. The internal energy of a system would always be expressed in this book by the symbol, U . In a system of constant composition, the magnitude of U will depend upon the thermodynamic variables (P , V , T), any two of which may be regarded as independent variables (sec. IV.2).

Thus, $U = f(P, T)$; or $U = f_1(P, V)$; or $U = f_2(T, V)$.

So, the internal energy becomes a property of the system entirely defined by its thermodynamic parameters. Whenever the system will be in the same thermodynamic state, its internal energy will have the same magnitude. The internal energy U is thus a single-valued function of the thermodynamic state of the system. Such functions, whose magnitudes are governed only by the state of the system, and nothing else, are termed *characteristic functions* or characteristic properties of the system.

It is true that, in most cases, it would not be possible to exactly evaluate the amount of the internal energy of the systems studied. That the systems possess internal energy is enough and is of vital importance in thermodynamics. Its implication would be fully realised from the First Law.

Internal Energy Change in a Cyclic Process. When a system changes from one thermodynamic state A to another thermodynamic state B , its internal energy U will also change. Let U_A and U_B be the respective internal energies in state A and state B . U_A and U_B will depend on the parameters only of the two different states. Then, the change in the internal energy $U_B - U_A$, represented by ΔU , will be governed only by the magnitudes of the variables in the initial state A and the final state B . ΔU will thus be independent of the *process*, or as very often called the *path*, by which the transformation has been carried out. A particular change of a given system may be effected by different processes or paths, but ΔU would be the same. To illustrate, a system of carbon and oxygen may be directly converted into carbon dioxide or through the intermediate formation of carbon monoxide, but ΔU in both the cases would be the same, provided the pressure, temperature, etc. in the initial and final states be the same in both cases.



Now, if a system suffers a series of changes so as to come back to the original initial state, the system is said to have completed a cycle. The series of processes, as a consequence of which the system reverts to its initial state, is called a *cyclic*

process or a cycle. In such a case, the internal energy of the system assumes its original magnitude, irrespective of what might have happened to the system meanwhile or previously. The internal energy of the system is independent of its previous history but is defined by the variables of the system at the moment. On the other hand, if all the internal energy changes (ΔU) in the different stages of the cyclic process be summed up, these would vanish, i.e., $\Sigma \Delta U = 0$,

or represented as, $\oint dU = 0$.

[The circle on the integral denotes a complete cyclic process.]

The changes of a system can be effected in different ways. If a change takes place in such a way that the temperature throughout remains unaltered, it is called an *isothermal* process.

On the other hand, the change of a thermally insulated system, enclosed by adiabatic walls through which heat exchange with the surroundings is not permissible, is called an *adiabatic* process.

IV.5. Some Simple Mathematical Formulae. A few simple formulae from calculus will have to be used very often in our subsequent discussion. A previous acquaintance with their distinctive forms would be convenient.

A. Partial derivatives. Suppose a quantity l is a function of two independent variables m and n , i.e.,

$$l = f(m, n)$$

Then, we can write $\Delta l = \left(\frac{\partial l}{\partial m} \right)_n \Delta m + \left(\frac{\partial l}{\partial n} \right)_m \Delta n$.

If the co-ordinates m and n change then the magnitude of l also will change. The derivative $\left(\frac{\partial l}{\partial m} \right)_n$ indicates the rate of change of l with change of m , when n remains constant.

The subscripts n, m at the right-hand bottom indicate their constancy during the changes of the rest. Hence the term $\left(\frac{\partial l}{\partial m} \right)_n \Delta m$ would obviously represent the change in the magnitude of l due to change Δm in m at constant n . Similarly, the second term $\left(\frac{\partial l}{\partial n} \right)_m \Delta n$ denotes the change in the value of l due to change Δn in n at constant m . Since the value of l depends only on the variables m and n , the sum of the two terms would represent the total change Δl of the value of l when m changes by Δm and n by Δn .

Now, suppose, there is a relation between three quantities x, y and z , such that

$$f(x, y, z) = 0.$$

So, we have $x = \psi(y, z)$ $y = \phi(z, x)$

As before we can write,

$$\Delta x = \left(\frac{\partial x}{\partial y} \right)_z \Delta y + \left(\frac{\partial x}{\partial z} \right)_y \Delta z \quad \dots (i)$$

$$\text{and} \quad \Delta y = \left(\frac{\partial y}{\partial z} \right)_x \Delta z + \left(\frac{\partial y}{\partial x} \right)_z \Delta x \quad \dots (ii)$$

Substituting (ii) in (i), we have

$$\begin{aligned} \Delta x &= \left(\frac{\partial x}{\partial y} \right)_z \left[\left(\frac{\partial y}{\partial z} \right)_x \Delta z + \left(\frac{\partial y}{\partial x} \right)_z \Delta x \right] + \left(\frac{\partial x}{\partial z} \right)_y \Delta z \\ &= \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z \Delta x + \left[\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x + \left(\frac{\partial x}{\partial z} \right)_y \right] \Delta z \quad \dots (iii) \end{aligned}$$

Now, equation (iii) is generally true for all values of x, y and z . Let us consider x and z as independent variables so that Δx and Δz may have any value.

(a) Suppose $\Delta z = 0$ and $\Delta x \neq 0$.

Then
$$\Delta x = \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z \Delta x.$$

or
$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z = 1 \quad \dots (IV.1)$$

or
$$\left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial x} \right)_z} \quad \dots (IV.2)$$

(b) Suppose $\Delta x = 0$, and $\Delta z \neq 0$, then from (iii),

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x + \left(\frac{\partial x}{\partial z} \right)_y = 0$$

or
$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x = - \left(\frac{\partial x}{\partial z} \right)_y = -1 / \left(\frac{\partial z}{\partial x} \right)_y \quad \dots \text{from (IV.2)}$$

i.e.,
$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1 \quad \dots (IV.3)$$

Illustrations : An equation of state can be represented as

$$f(P, V, T) = 0$$

i.e., $V = f_1(P, T); P = f_2(V, T); T = f_3(P, V).$

Hence, we have,

$$\left. \begin{aligned} \Delta V &= \left(\frac{\partial V}{\partial P} \right)_T \Delta P + \left(\frac{\partial V}{\partial T} \right)_P \Delta T \\ \Delta P &= \left(\frac{\partial P}{\partial V} \right)_T \Delta V + \left(\frac{\partial P}{\partial T} \right)_V \Delta T \\ \Delta T &= \left(\frac{\partial T}{\partial P} \right)_V \Delta P + \left(\frac{\partial T}{\partial V} \right)_P \Delta V \end{aligned} \right\} \quad \dots (iv)$$

further
$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{1}{(\partial T / \partial P)_V}, \text{ etc.} \quad \dots (v)$$

and
$$\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T = -1 \quad \dots (vi)$$

Let us consider 1 gm-mole of an ideal gas, when $PV = RT$, then,

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V}; \quad \left(\frac{\partial T}{\partial V} \right)_P = \frac{P}{R}; \quad \left(\frac{\partial V}{\partial P} \right)_T = \frac{-RT}{P^2}; \quad \left(\frac{\partial T}{\partial P} \right)_V = \frac{V}{R}$$

Now applying (v),
$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V} = \frac{1}{V/R} = \frac{1}{\left(\frac{\partial T}{\partial P} \right)_V}.$$

Again
$$\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T = \frac{R}{V} \cdot \frac{P}{R} \cdot \frac{-RT}{P^2} = -\frac{RT}{PV} = -1$$

From equation (iv), the total differential volume of an ideal gas is

$$\begin{aligned} \Delta V &= \left(\frac{\partial V}{\partial P} \right)_T \Delta P + \left(\frac{\partial V}{\partial T} \right)_P \Delta T \\ &= \frac{-RT}{P^2} \cdot \Delta P + \frac{R}{P} \cdot \Delta T \end{aligned}$$

The internal energy is a characteristic property and hence, $U = f(P, T)$

$$\text{or} \quad \Delta U = \left(\frac{\partial U}{\partial P} \right)_T \Delta P + \left(\frac{\partial U}{\partial T} \right)_P \Delta T$$

Such expressions would very often be used.

B. Perfect Differentials As before, let $z = \psi(x, y)$.

It is presumed that z is a single-valued quantity such that its magnitude at any moment or in any given state is solely determined by the instantaneous values of x and y at that moment in the given state. If the variables change, the magnitude of z may change and this change dz is a *perfect* or *complete differential*. To make it clear, let us represent graphically the variables x and y along two axes at right angles (Fig. IV.2). At the point P (with co-ordinates x, y), the magnitude of z is z_1 . Again at the point Q (co-ordinates x', y') the magnitude of z is z_2 . Then $dz = (z_2 - z_1)$ will always have the same value determined by x, y, x', y' ; dz is a perfect differential and dz is independent of the path of transformation from P to Q . It is also obvious that if a change from P to Q is brought about by one path (say I) and the reverse change is effected by another path (say III), the magnitude of z will come back to the same value, defined by x, y at P . Hence for a complete cyclic process, of transformation reverting to the original state,

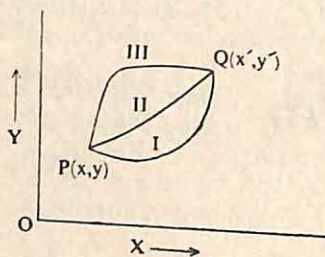


FIG. IV.2

$$\begin{aligned} \Sigma \Delta z &= 0 \\ \text{or} \quad \oint dz &= 0 \end{aligned}$$

This can be considered from another direction. Let P and Q in [Fig. IV.3], have co-ordinates (x, y) and $(x + \Delta x, y + \Delta y)$, respectively. Suppose the transition from P to Q can be effected in two ways along PRQ or PSQ .

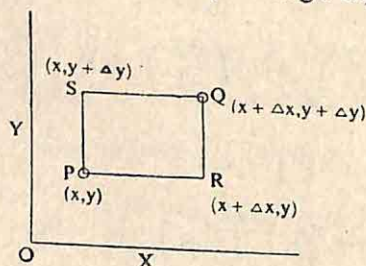


FIG. IV.3

In the path PRQ , we first change the variable x to $x + \Delta x$, y remaining constant to reach the point R . Then x being kept constant as $x + \Delta x$, the variable y is altered to $y + \Delta y$, till Q is reached. Then, at R , the value of z would be $z + \left(\frac{\partial z}{\partial x} \right)_y \Delta x$. So, at Q ,

$$z + \Delta z = z + \left(\frac{\partial z}{\partial x} \right)_y \Delta x + \frac{\partial}{\partial y} \left[z + \left(\frac{\partial z}{\partial x} \right)_y \Delta x \right] \Delta y$$

Similarly, if we follow the path PSQ , the co-ordinates, at the point S , would be $x, y + \Delta y$ and the value of z at the point S would be $z + \left(\frac{\partial z}{\partial y} \right)_x \Delta y$. So, when the point Q is reached,

$$z + \Delta z = z + \left(\frac{\partial z}{\partial y} \right)_x \Delta y + \frac{\partial}{\partial x} \left[z + \left(\frac{\partial z}{\partial y} \right)_x \Delta y \right] \Delta x$$

If dz is to be a perfect differential, the two expressions must be equal to one another, hence

$$\begin{aligned} z + \left(\frac{\partial z}{\partial y} \right)_x \Delta y + \left(\frac{\partial z}{\partial x} \right)_y \Delta x + \frac{\partial^2 z}{\partial x \partial y} \cdot \Delta x \cdot \Delta y \\ = z + \left(\frac{\partial z}{\partial x} \right)_y \Delta x + \left(\frac{\partial z}{\partial y} \right)_x \Delta y + \frac{\partial^2 z}{\partial y \partial x} \cdot \Delta x \cdot \Delta y \end{aligned}$$

$$\text{or,} \quad \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$$

That is, if dz is a perfect differential, then $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$.

Conversely, we can conclude that dz will be a perfect differential when it is found that

- (i) z is a single-valued function depending entirely on the instantaneous values of x and y ; or,
- (ii) dz between any two specified points or states is independent of the path of transition; or,
- (iii) $\oint dz$ for complete cyclic process is equal to zero, or,
- (iv) $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$ i.e., the second differentials of z with respect to x and y

carried out in either order become equal to one another.

Illustrations : (a) Let us take a system containing a gm-mole of an ideal gas, then, $T = f(P, V)$. Hence, by definition dT is a perfect differential. It can be proved as follows :

$$PV = RT.$$

$$\text{or} \quad \left(\frac{\partial T}{\partial V} \right)_P = \frac{P}{R}; \quad \text{i.e.,} \quad \frac{\partial^2 T}{\partial P \partial V} = \frac{1}{R}$$

$$\text{Again,} \quad \left(\frac{\partial T}{\partial P} \right)_V = \frac{V}{R}; \quad \text{i.e.,} \quad \frac{\partial^2 T}{\partial V \partial P} = \frac{1}{R}$$

$$\text{Therefore,} \quad \frac{\partial^2 T}{\partial V \partial P} = \frac{\partial^2 T}{\partial P \partial V}$$

Hence, dT is a perfect differential.

(b) We know internal energy U of any given system depends only on the state of the system and, hence, is dependent on any two of the three common variables, (say, P and T). dU is then a perfect differential. We can therefore say that

$$\frac{\partial^2 U}{\partial P \partial T} = \frac{\partial^2 U}{\partial T \partial P}$$

$$\text{or} \quad \oint dU = 0 \text{ (for any cyclic process).}$$

There are various other thermodynamic functions such as heat-content, entropy etc., which depend only on the thermodynamic states and therefore, their small changes like dH , dS , etc. are perfect differentials.

THE FIRST LAW

IV.6. The First Law of Thermodynamics. In the forties of the last century it came to be generally believed that heat was a form of energy and heat and work are interchangeable. Mayer, a German physician, was probably the first to announce in an obscure journal that there is a quantitative relation between the two forms, heat and work, when interchange takes place. From some crudely arranged experiments in those early days, he could even suggest an astonishingly accurate value of the equivalence between the two forms of energy.

Meanwhile Joule had carried out very thorough and elaborate investigations of this problem and clearly demonstrated from his experiments that the same

quantity of heat would always be produced by the performance of a given amount of work, irrespective of the nature of process in which the work is performed or the substance used in the performance. In other words, there is a strict quantitative relation between the work spent and the heat produced. For the production of unit quantity of heat (measured in calories) we shall have to perform a definite amount of work (measured in ergs). Hence, if

$$x \text{ calories of heat} \equiv y \text{ ergs of work}$$

then,

$$nx \text{ calories of heat} \equiv ny \text{ ergs of work}$$

There is a constant proportionality between heat and work. So,

$$W = JQ$$

where J is the constant of proportionality between the work performed W and the heat produced Q . J is the amount of work required to produce unit quantity of heat and is called the mechanical equivalent of heat.

Joule, in his experiments, carried out the performance of work in diverse ways. The work was done by (a) agitating paddle wheels in a mass of water or mercury, (b) rubbing iron rings under mercury, (c) compressing air in narrow tubes, (d) passing electricity through a wire of known resistance, etc. The heat produced was measured from the specific heats of the materials used and the rise of temperature due to friction or passage of electricity. Later on, many other workers carried on the determination of the value of J with considerable accuracy amongst which the experiments of Rowlands, Callender and Barnes, Laby and Hercus, are specially notable.* The accepted value of J is 4.1858×10^7 ergs per calorie.

This relation between heat and work, which is the origin of the first law, may be enunciated as "*If or whenever, heat is obtained from work, the amount of heat produced is proportional to the work spent, or conversely, if heat is transformed into work, there is a proportionality between the work obtained and the heat disappeared.*"

Not only heat can be converted into work but different forms of energy are all interconvertible into one another. A given quantity of electrical energy, comparatively easily measurable, was found to be equivalent to a definite amount of heat or mechanical work. It was soon realised that such equivalence did not only exist between heat and work but between any two forms of energy. And if,

$$x \text{ units of energy } A \equiv y \text{ units of energy } B$$

then,

$$mx \text{ units of energy } A \equiv my \text{ units of energy } B$$

The proportionality between quantities of two given forms of energy is universally constant and the constancy of this proportionality is the essence of the first law.

Helmholtz gave a clear expression of this experimentally realised experience. He stated that the different forms of energy are interchangeable but when a quantity of one kind of energy disappears an equivalent amount of another kind makes its appearance. This is a more general statement of the first law of thermodynamics. Since the disappearance of an amount of energy causes appearance of an equivalent amount of energy of another form, neither more nor less, we are compelled to accept that energy cannot be completely annihilated nor can it be created from nothing. Clausius, therefore, enunciated that varied changes and transformation might occur but the total energy of the universe must remain constant.** Hence, the first law of thermodynamics is really the *law of conservation of energy*.

Algebraic formulation. Consider a system in a state A having an internal energy U_A undergoing a change to a state B . During the transformation (physical, chemical or mechanical) let the system absorb a small quantity of heat Δq (say), then the net amount of energy of the system would become $U_A + \Delta q$. In the process

*For details of these experiments, Robert's Heat & Thermodynamics (Blackie & Co.) may be consulted.

**In the thermal processes in the stars or in atomic energy production, the Einstein's equation is to be invoked ($E = mc^2$) and the laws of conservation of mass and of energy must be combined.

of transformation, the system might have also performed some work ΔW , electrical or mechanical or of any other type. If U_B be the internal energy of the system at state B , then the net energy after transformation would amount to $U_B + \Delta W$.

From the principle of conservation of energy, we clearly see

$$U_A + \Delta q = U_B + \Delta W$$

The usual convention is that the work done by the system (and therefore received by the surroundings) is taken as positive while the work done on the system by the surroundings is considered negative. Any form of energy other than heat which would leave or enter into a system is categorically included in the term *work*.

The increase in the internal energy of a system is regarded as positive and its decrease negative.

The heat entering into a system *i.e.*, gained by the system is conventionally regarded as positive and so heat lost by the system to the surroundings is taken as negative.

We see then, $\Delta q = U_B - U_A + \Delta W = \Delta U + \Delta W$
or in the differential form ; $dq = dU + dW$. . . (IV.4)

That is, heat taken up by a system would be equal to the internal energy-increase of the system and the work done by the system. This is the algebraic statement of the first law.

A few comments may be made on this equation.

(a) In an isolated system there is no heat exchange with surroundings (adiabatic process), $dq = 0$

$$\therefore dU + dW = 0, \text{ or } dW = -dU$$

The work performed, irrespective of its nature, by an isolated system will be equal to the internal energy decrease. This enables us to define the internal energy of the system as a property whose change is measured by the amount of work performed by or on the system under adiabatic conditions.

(b) In a cyclic process, $\oint dU = 0$.

$$\text{Hence, } \oint dq = \oint dU + \oint dW$$

$$\text{or } \oint dq = \oint dW$$

The total work obtained is equal to the net heat supplied and no excess work can be obtained.

(c) In a non-isolated system, permitting heat-transfers with the surroundings, the system gains heat (dq) and performs work (dW). For the system,

$$dU = dq - dW$$

If we consider the surroundings only, it loses dq amount of heat but receives dW units of work. The internal energy change of the surroundings will then be

$$dU' = dW - dq$$

Therefore,

$$dU = -dU'$$

The gain in internal energy of the system is counterbalanced by the loss in the same of the surroundings, or,

$$dU + dU' = 0.$$

The net change in the internal energies of the system and the surroundings taken together would be nil.

We often require different forms of energy for different purposes. We need electrical energy for the light-bulb but mechanical energy for driving a car or a train. This necessitates conversion of one kind of energy into another. The transformation into the desired form may not often be directly done. For example, coal contains inherently a lot of internal energy. During burning

this energy functions as chemical energy and yields heat. The heat (may be partly) is converted, by radiation, conduction etc. into the mechanical energy of steam, which moves the engine to pull a train. Or, the mechanical energy thus produced may be made to run a generator to produce electrical energy, to be used for different purposes. The electrical energy can also be made to charge a storage cell and is thus locked up in the chemical form. That means, some energy originally present in the coal is now in the storage battery. It may be questioned as to how the coal acquired the chemical energy. The radiations from the sun were picked up in the remote past by the living plants in a process called photosynthesis converting a portion of the radiant energy into chemical energy. These plants by continuous process of thermal and pressure-changes went beneath the soil to be transformed into coal and petroleum. The origin is then the solar radiation.

IV.7. dQ and dW are not Perfect Differentials. In dealing with eqn. IV.4 of the first law, it should be clearly realised that in the transformation of a system from a given state I to another given state II, the internal energy change dU is independent of the process in which the transformation is effected, i.e., dU is a perfect differential. But this cannot be said of either dQ , the heat transfer or dW , the work performed. For example, when the reaction between zinc and copper sulphate is carried out in a flask, a quantity of heat dQ is evolved. But if the same reaction is effected in a different way in the arrangement of a voltaic cell practically no heat is evolved (i.e., $dQ = 0$), internal energy-change appears as electrical work. Hence, heat-transfer dQ depends on the path. It is evident in the first path no work was available but in the second path considerable electrical work dW is obtained. The work term dW also then depends on the path. We might also say, since dU is a perfect differential and as it is equal to $dQ - dW$ of which dQ is not a perfect differential, hence dW cannot also be a perfect differential.

We can cite other instances. When a quantity of an almost ideal gas enclosed in a cylinder immersed in a thermostat is allowed to expand from a volume V_1 to a volume V_2 , it performs work $P(V_2 - V_1)$, where P is the constant external pressure. If this P is made once half an atmosphere and at another instance almost equal to zero, the dW in the two instances would be different for the same volume-change of the ideal gas at constant temperature. Again, if a mixture of oxygen and gasoline be burnt in an enclosed vessel of constant volume, a large quantity of heat ΔQ will be available, but if the same change be carried out in the cylinder of an engine, the products of combustion will push out the piston and perform some work and evolve also some quantity of heat. All these point to the conclusion that dW or dQ are not perfect differentials. But nevertheless $dQ - dW$ is a perfect differential.

IV.8. Reversible and Irreversible Processes. The change of a system from one state to another may occur either in a reversible or in an irreversible way. In a reversible process, the change of the system is allowed to happen slowly in minute quantities until the whole of the specified change is achieved. In an ideally reversible process, the change must occur in successive stages of infinitesimal quantities. The small changes should be carried out in such a way that, throughout the transition, the system must be maintaining virtual thermodynamic equilibrium, at each of the small stages. Moreover a reversible process must be such that the system may change in the opposite direction back to the initial condition along the same path and the magnitudes of the changes of the thermodynamic quantities in the different stages will be the same as in the forward direction but opposite in sign. Suppose, the expansion of a gas from volume V_1 to V_2 has been effected in 100 stages both in the forward and backward directions. Then if the heat-change be $-dq$ and the work done be $+dW$ in the 10th stage in the forward process, the heat-transfer and work would be $+dq$ and $-dW$ in the 91st stage in the backward transformation.

Suppose we have a system in which heat-transfer is occurring. A reversibility of the process implies that the surroundings which delivers the heat to the system must have a temperature T_1 , infinitesimally higher than the temperature T of the system. Likewise, if heat is to flow reversibly from the system at T to the surroundings, then T should be slightly above T_1 , the temperature of the surroundings.

Again suppose a gas is enclosed in a cylinder with a piston and kept in a constant temperature bath. The pressure over the piston is P . The gas will expand if the pressure P is very slightly lowered to P' . Let the work of expansion be ΔW . If now the new pressure be raised slightly, back to P , the gas will contract. It can be shown that the work now performed on the gas during contraction will be the same as received from the system during expansion. Such a change would be regarded as a reversible one.

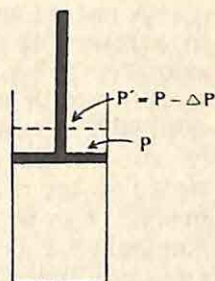


FIG. IV.4

A truly reversible process, has to be carried out in infinitesimal amounts and, hence, would require infinite time. In practice, the small changes in a process have definite magnitudes and are thus only close approximations at the best to a true reversible process. A strictly reversible process is thus purely a concept, nevertheless it is extremely useful in analysis of our problems of energy-changes.

An irreversible process is one which occurs suddenly or spontaneously without the restriction of occurring in successive stages of infinitesimal quantities. The system would also not remain in virtual equilibrium during the transition. The system after undergoing a change will not have the tendency to return to the initial state by itself. If the change be reversed and the system is made to go back to the initial state, the work (dW) in the forward direction and in the backward process would be unequal. It is important to remember that if the initial and final stages be specified, the internal energy change would always be the same, whether the process has been effected reversibly or irreversibly. In an irreversible process, since work terms (dW) in the two opposite directions are unequal, the heat-transfers (dQ) would also be unequal.

Many processes occur in nature spontaneously. These spontaneous processes happen unidirectionally and certainly not in successive stages of equilibria in minute quantities of transformation. Natural processes are therefore all irreversible.

Suppose water in a beaker is heated from 20°C by heating over a Bunsen flame. This process is irreversible, because the temperature of the flame is very high and the water near the bottom of the beaker will be more quickly heated than the rest. In consequence convection and turbulence would start. As such, the equilibrium is disturbed and the change is not reversible.

The water from the slopes of the Himalayas flows down the Ganges into the Indian Ocean. Such natural flow of a liquid downwards is spontaneous and is irreversible. The water in the Indian Ocean will of itself never go up the hill. If the water is pushed up from the Ganges by external agencies, the work to be done far exceeds the work received during its downward flight. Hence the process is irreversible.

A gas like ammonia brought in contact with water will spontaneously be absorbed by water forming a solution, producing heat and particularly no work. Of itself, the solution would not separate back into the two components water and the gas. A lot of work has to be performed to separate these two from the solution.

Carbon, set fire to, burns in oxygen producing carbon dioxide and a quantity of heat. If the heat received thus be restored to carbon dioxide, the latter will not revert back to carbon and oxygen. The process thus carried out is irreversible. Similarly, heat produced due to friction in the motion of two bodies, the diffusion of two gases into one another, or flow of heat from a body at higher temperature to that at a lower temperature, are all irreversible changes.

A reversible process is that in which the opposite changes can be effected along the same path with heat-changes and works performed being the same though opposite in sign, and as such the process has to be carried out in successive stages of equilibrium in small amounts. An irreversible process would not satisfy these conditions.

The fact that the process is irreversible does not mean that the system cannot be restored to the original state. The water that has come down to the ocean can be taken back to the top of the hill, the carbon dioxide can be decomposed back to carbon and oxygen, etc. But such reversals would involve work by the surroundings or external agencies greater than that was obtained during the forward changes.

A change carried out naturally in an irreversible way may also be performed in a reversible fashion, but that would need some special arrangement. For example, the beaker containing water to be heated from 20° to 30°C may be placed successively in thermostats of temperatures 20.1° , 20.2° , 20.3° , 20.4° and so on, until 30°C is reached. At every stage, the system must be allowed to attain equilibrium. The smaller the temperature differences of the thermostats, the more ideal would be the reversibility. The process of irreversible solubility of ammonia gas in water may be performed in the following way to make it a reversible one. The ammonia gas may first be expanded to an infinitely large volume, by reducing the pressure. The gas at extremely low pressure be brought in contact with water when extremely slowly the gas will enter the liquid. Subsequently, by increasing the pressure in infinitesimal amounts the gas may be completely dissolved.

IV.9. Work in a Reversible Process. (i) *Expansion of a gas.* Suppose we have a quantity of gas in a cylinder enclosed by a frictionless piston (Fig. IV.5). The whole cylinder is kept immersed in a large constant-temperature bath at $T^\circ(\text{Abs})$.

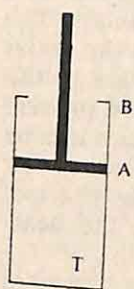


FIG. IV.5

Any change that would occur to this system would thus be isothermal. There is also a latch in the cylinder at the top (B) and the piston is at B, is, suppose V_2 . To start with, the gas occupies a volume V_1 and the piston is at the point A, the equilibrium pressure over the piston being P_1 . The aim is to expand the gas from volume V_1 to volume V_2 by reducing the pressure. This can be done in various ways. We can make the pressure over the piston arbitrarily anything, say 0 (zero), $\frac{1}{2}P_1$, $\frac{1}{3}P_1$, etc., and the piston will immediately move up. When pressure is zero, work would be nil. If pressure is $\frac{1}{2}P_1$, work would be $\frac{1}{2}P_1(V_2 - V_1)$. If pressure is $\frac{1}{3}P_1$, work would be $\frac{1}{3}P_1(V_2 - V_1)$ and so on. In fact, we may get different amounts of work from the same change. All these processes obviously are irreversible.

But we can also carry out the process in the following way. Let us reduce the pressure P_1 by an infinitesimal amount ΔP , i.e., let the pressure be $P_1 - \Delta P$. Let the consequent minute volume-increase be ΔV . Then the work done by the system would be $(P_1 - \Delta P) \Delta V = P_1 \Delta V$, the term $\Delta P \Delta V$ being negligibly small. The new pressure is again very slightly reduced and a little more expansion effected. This process may be repeated and thus by infinite number of successive steps, the gas may expand from volume V_1 to V_2 . Let the final pressure be P_2 when the volume is V_2 . At every step a small amount of work is obtained given by $P \Delta V$, where the pressure (P) continuously changes from P_1 to P_2 . Hence total work is given by.

$$\Delta W = \int_{V_1}^{V_2} P dV$$

We must remember that P has also been changing during the expansion continuously. If the system contains n gm-moles of the gas and the gas be supposed to be an ideal one, then

$$\Delta W = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1}$$

For the isothermal expansion of one gm-mole of gas at temperature $T^\circ \text{ Abs.}$

$$\Delta W = RT \ln \frac{V_2}{V_1}$$

Since

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \text{ at const. temperature, we have,}$$

$$\Delta W = RT \ln \frac{P_1}{P_2}$$

The change has been carried out in successive stages of infinitesimal amount and therefore, this is a reversible process. Hence the work in the *isothermal reversible expansion* of one mole of ideal gas is

$$\Delta W = RT \ln \frac{V_2}{V_1} \quad \dots (IV.5)$$

This work is necessarily the product of the force and the displacement. The displacement in this case is specified, namely $(V_2 - V_1)$. Hence, the greater the magnitude of the force or pressure, the greater would be the magnitude of work. If the pressure over the piston were made greater than $(P_1 - \Delta P)$, there obviously would be no expansion. Therefore if we want to have the expansion as desired, $(P_1 - \Delta P)$ is the maximum that could be applied. So, the work obtained in equation (IV.5) is the maximum. If the pressure over the piston were made appreciably less, instead of infinitesimally smaller than the gas pressure, the work would be evidently less than that obtained above and the process also would be more irreversible. We are therefore led to conclude that the work in the reversible process is the *maximum* and is greater than that in the irreversible process.

Suppose we carry out a small expansion of the same gas in two ways. Firstly, we change the volume as before until the pressure is P_2 , the process is reversible and the reversible work is given by,

$$\Delta W_r = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2}$$

Secondly, we reduce the pressure over the piston at once to P_2 which would be the equilibrium pressure of the gas when the volume is V_2 , then the gas would immediately expand against a constant pressure P_2 , the process is irreversible and the irreversible work

$$\Delta W_{ir} = P_2(V_2 - V_1) = P_2 \left[\frac{RT}{P_2} - \frac{RT}{P_1} \right] = RT \left[1 - \frac{P_2}{P_1} \right]$$

$$\begin{aligned} \text{Then, } \Delta W_r - \Delta W_{ir} &= RT \ln \frac{P_1}{P_2} - RT \left[1 - \frac{P_2}{P_1} \right] \\ &= RT \frac{P_1 - P_2}{P_2} - RT \frac{P_1 - P_2}{P_1} \quad (\text{for small changes}) \\ &= RT(P_1 - P_2) \left[\frac{1}{P_2} - \frac{1}{P_1} \right] = \frac{RT}{P_1 P_2} (P_1 - P_2)^2 = +ve \text{ quantity} \end{aligned}$$

Hence,

$$\Delta W_r > \Delta W_{ir}$$

The work in a reversible process is greater than that in an irreversible process.

Let us now return to the same system when the gas has expanded to volume V_2 and pressure P_2 . It can now be easily seen that if we continue to increase the pressure by infinitesimal amounts in successive stages until the volume becomes V_1 , and therefore, pressure P_1 , the work done on the system would be

$$\Delta W = \sum P \Delta V = \int_{V_2}^{V_1} P dV = RT \ln \frac{V_1}{V_2} = -RT \ln \frac{V_2}{V_1}.$$

That is, the work term is the same with a reversal of sign. Hence in a complete reversible cycle of expansion and contraction at constant temperature, the net work would be zero.

Or, in an *isothermal reversible cyclic process*, $\oint dW = 0$

This is not only true in the expansion of a gas but in other types of changes as well. Suppose a voltaic battery is used to perform electric work, maximum work will be obtained when currents are drawn in exceedingly small quantities thereby

reducing the e.m.f. in successively small amounts, so that e.m.f. remains as high as possible while yielding the work. The same work will also be involved in charging the battery.

It is seen that

- (i) *A change carried out in a reversible way yields maximum work. Conversely, in order to obtain maximum work the change must be effected in a reversible fashion.*
 (ii) *The net work in an isothermal reversible cyclic process is zero.*

If the system contains one mole of a van der Waals' (real) gas, the work of isothermal expansion would be given by

$$\Delta W = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \left(\frac{RT}{V-b} - \frac{a}{V^2} \right) dV,$$

$$\Delta W = \left[RT \ln(V-b) + \frac{a}{V} \right]_{V_1}^{V_2} = RT \ln \frac{V_2-b}{V_1-b} + a \left[\frac{1}{V_2} - \frac{1}{V_1} \right] \quad (\text{IV.6})$$

Problems. (a) Calculate the max. work done when the pressure on 10 gms. of hydrogen is reduced from 20 to 1 atmospheres, the temperature remaining constant at 0°C . The gas is supposed to behave ideally.

The work of expansion of n gm-moles of gas from pressure P_i to P_f

$$W = nRT \ln \frac{P_i}{P_f} = 2.303 \times 5 \times 8.31 \times 273 \log \frac{20}{1} = 33960 \text{ joules.}$$

Since

$$n = \frac{10}{2} = 5 \text{ moles}$$

(b) Isothermally at 27°C , one mole of a van der Waals' gas expands reversibly from 2 litres to 20 litres. Calculate the work done if $a = 1.42 \times 10^{12}$ dynes-cm⁴ per mole and $b = 30$ c.c. per mole.

By equation IV.6, work = $RT \ln \frac{V_2-b}{V_1-b} + a \left[\frac{1}{V_2} - \frac{1}{V_1} \right]$

$$W = 2.303 \times 8.31 \times 10^7 \times 300 \log \frac{20-.03}{2-.03} + 1.42 \times 10^{12} \left[\frac{2000-20000}{20000 \times 2000} \right] \text{ ergs}$$

$$= 5677 \times 10^7 \text{ ergs} = 5677 \text{ joules.}$$

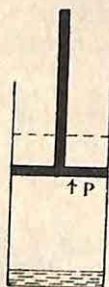


FIG. IV.6

(ii) *Vaporisation of a liquid.* Consider a system containing a liquid in equilibrium with its vapour at a constant temperature and hence having constant vapour pressure P in a cylinder provided with a frictionless piston. If the piston is slightly raised at constant temperature, immediately a little liquid would vaporise to keep the vapour pressure constant. In this way let V_l volume of liquid be vaporised to produce V_g volume of vapour. This process takes place against constant pressure P throughout and the net volume-change of the system is $(V_g - V_l)$. Then the work obtained is

$$\Delta W = P \Delta V = P(V_g - V_l)$$

In most cases, V_l is negligible compared to V_g and further if the vapour is supposed to obey ideal gas laws then

$$\Delta W = PV_g = P \cdot \frac{RT}{P} = RT \text{ (for 1 gm-mole)} \quad \dots (\text{IV.7})$$

(iii) *Addition of solvent to a solution.* (a) If we simply add some solvent to a given solution, scarcely any work would be obtained and the process is irreversible. But a reversible work may be derived in the following way.

Consider two cylinders with pistons as before, one containing pure solvent and the other containing solution, both in equilibrium with the vapour of the solvent (FIG. IV.7). Both are at the same temperature T° Abs. The vapour pressure over the solvent is P_0 and that over the solution P_1 . It is known $P_0 > P_1$. Then,

Then, let Δx gm-moles of pure solvent be vaporised reversibly at the same temperature, the work, neglecting volume of the liquid (eqn. IV.7),

$$\Delta W_1 = P_0 \Delta V = \Delta x RT.$$

Δx gm-moles of vapour is now separated from the cylinder and allowed to undergo expansion until the pressure becomes P_1 , isothermally. The work involved in this process, given by equation (IV.5) assuming the vapour as an ideal gas, would be

$$\Delta W_2 = \Delta x RT \ln \frac{P_0}{P_1}$$

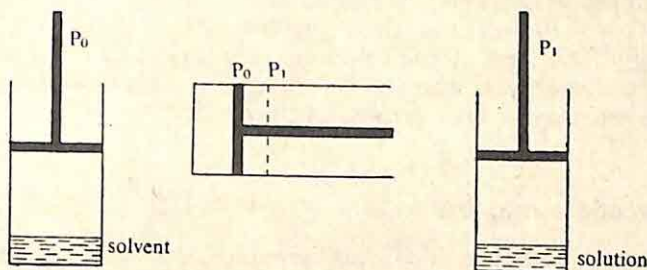


FIG. IV.7

The vapour, now at pressure P_1 , is introduced in the cylinder containing the solution and the piston is gradually lowered reversibly until Δx gm-moles of vapour condense into the solution. The work, reversible and opposite to that of vaporisation, would be

$$\Delta W_3 = P_1 \Delta V = \Delta x RT.$$

The net work, therefore,

$$\Delta W = \Delta W_1 + \Delta W_2 + \Delta W_3 = \Delta x RT \ln \frac{P_0}{P_1}$$

It is presumed that such small addition of the solvent would not materially alter the concentration of the solution. If 1 gm-mole of solvent be added to a very large volume of solution, then

$$\Delta W = RT \ln \frac{P_0}{P_1} \quad \dots (IV.8)$$

If instead, a concentrated solution (conc. c_2 and vap. pressure P_2) be diluted by a less concentrated solution (conc c_1 and vap. pressure P_1), then it can be shown that the net work would be

$$\Delta W = RT \ln \frac{P_2}{P_1} \quad \dots (IV.9)$$

(iv) *Dilution of a solution.* We shall next consider the work involved in diluting a solution from a higher to a lower concentration. Consider an arrangement as shown in Fig. IV.8. A cylinder containing a solution (conc. C_1) and pure solvent is enclosed by two pistons at the two ends, the solvent being separated from the solution by a semipermeable membrane AB. The membrane only allows solvent to pass through. The temperature T° Abs is kept constant. The osmotic pressure of the solution is π and the piston on the top exerts a pressure π just sufficient to prevent osmosis. If the pressure in the piston is slightly lowered, a small amount of the solvent would enter. Let this infinitesimal lowering be successively continued until ΔV c.c of the solvent enters the solution reducing its osmotic pressure to π' and concentration to C_2 . The work done by the system,

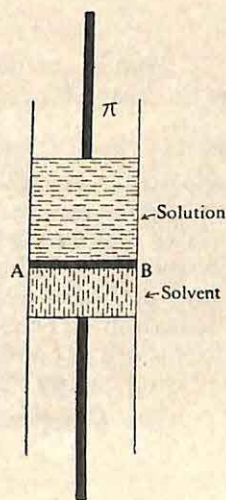


FIG. IV.8

$$\Delta W = \int_{C_1}^{C_2} \pi dV$$

Now concentration, $C = \frac{1}{V}$; i.e., $dC = -\frac{1}{V^2}dV = -C^2dV$

$$\therefore \Delta W = \int_{C_1}^{C_2} CRT \left(-\frac{1}{C^2} \right) dC = -RT \int_{C_1}^{C_2} \frac{dC}{C} = RT \ln \frac{C_1}{C_2} \quad \dots \text{(IV.10)}$$

[It is assumed that osmotic pressure $\pi = CRT$. It will be proved later in connection with dilute solutions.]

IV.10. Heat Content or Enthalpy. The pressure and the volume of a system are thermodynamic co-ordinates and their product PV , we have seen, is expressed in units of energy. The sum of the two energy terms associated with the system, namely the internal energy U and the PV -energy, is universally represented by H and is called the *enthalpy* or *heat-content* of the system.

$$H = U + PV \quad \dots \text{(IV.11)}$$

$$\text{In the differential form, } dH = dU + PdV + VdP \quad \dots \text{(IV.12)}$$

If a system undergoes a change at *constant pressure*, the change in enthalpy,

$$dH_P = dU_P + PdV_P, \quad \dots \text{(IV.13)}$$

the suffix P is used to indicate constancy of pressure.

We know, U depends on the state of the system and P and V themselves specify the state, being thermodynamic co-ordinates. The heat-content H , therefore, depends only on the state. H is thus a characteristic function of the system and dH is a perfect differential. The magnitude of dH , for a given change of the system, will be independent of the path of the change.

$$\text{The first law states} \quad dQ = dU + dW$$

The work dW may be mechanical, electrical, chemical or of any other type. If we consider processes in which the entire work is mechanical i.e., expansion or contraction of the system, then dW would depend on the values of P and V . Further if the change of the system be carried out at constant pressure, then

$$dW_P = PdV_P \quad \dots \text{(IV.14)}$$

The change at constant volume would involve no mechanical work.

Hence from the first law for a change at constant pressure,

$$dQ_P = dU_P + dW_P = dU_P + PdV_P \quad \dots \text{(IV.15)}$$

Substituting (IV.13),

$$dQ_P = dH_P \quad \dots \text{(IV.16)}$$

That is, the increase in heat-content of a system during a given transformation is the heat absorbed during the process at const. pressure.

IV.11. Ideal Gases. Experiments conducted by Joule showed that if a gas be allowed to expand freely into a vacuum, there was practically no heat-change with the surroundings. An evacuated bulb was connected through a stop-cock to a vessel containing air. When the stop-cock was opened, the air passed into the evacuated bulb but there was no temperature change. The system did not lose or gain any heat. We now know that this experiment really corresponds to ideal behaviour. The expansion into a vacuum (where $P = 0$), involves no work. Therefore, both dQ and dW are zero. From the 1st Law, therefore, $dU = 0$. That is, the internal energy of a gas does not depend upon the volume.

But U depends upon temperature. Hence, at constant temperature,

$$\left(\frac{dU}{dT} \right)_T = 0 \quad \dots \text{(IV.17)}$$

This assumption is made for ideal gases. At constant temperature, the pressure varies with volume. Since for ideal gases,

$$\left(\frac{dU}{dV}\right)_T = 0, \quad \text{hence} \quad \left(\frac{dU}{dP}\right)_T = 0 \quad \dots (IV.18)$$

Further, we know, $H = U + PV$

$$\text{i.e.,} \quad \left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T$$

Ideal gases obey Boyles' Law ; hence $\left(\frac{\partial(PV)}{\partial P}\right)_T = 0$

$$\therefore \quad \left. \begin{aligned} \left(\frac{\partial H}{\partial P}\right)_T &= 0 \\ \left(\frac{\partial H}{\partial V}\right)_T &= 0 \end{aligned} \right\} \quad \dots (IV.19)$$

and consequently

Internal energy and heat-content of ideal gases are independent of pressure and volume.

IV.12. Heat Capacity. If a system is raised 1°C in temperature keeping the pressure constant, the amount of heat required is called the heat-capacity at constant pressure denoted by c_P . If one gm-mole of substance be taken as the system, the symbol used for molar heat-capacity at constant pressure is C_P .

$$\text{Hence} \quad C_P = \frac{\Delta Q_P}{\Delta T} = \frac{\partial Q_P}{\partial T}$$

$$\text{But from (IV.16),} \quad dQ_P = dH_P$$

$$\therefore \quad C_P = \frac{\partial H_P}{\partial T} = \left(\frac{\partial H}{\partial T}\right)_P \quad \dots (IV.20)$$

On the other hand, the amount of heat required to raise the temperature of a system by 1°C keeping its volume constant is called its heat-capacity at constant volume, denoted by c_V . The symbol C_V is used in the case of a gm-molecule.

As the volume is kept constant, no mechanical work is involved (we are not considering other types of work at present), i.e.,

$$dQ_V = dU_V$$

$$\text{Hence,} \quad C_V = \frac{\Delta Q_V}{\Delta T} = \frac{\partial Q_V}{\partial T} = \frac{\partial U_V}{\partial T} = \left(\frac{\partial U}{\partial T}\right)_V \quad \dots (IV.21)$$

The rate of change of heat-content at constant pressure with temperature is the heat-capacity at constant pressure. The rate of change of energy-content at constant volume with temperature is the heat-capacity at constant volume.

The two specific heats are not equal and the relationship between them can be easily deduced.

$$U = f(T, V)$$

$$\Delta U = \left(\frac{\partial U}{\partial T}\right)_V \Delta T + \left(\frac{\partial U}{\partial V}\right)_T \Delta V$$

$$\text{or} \quad \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\begin{aligned}
 \text{Then } C_P - C_V &= \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \\
 &= \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \\
 &= \left(\frac{\partial U}{\partial T} \right)_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \\
 &= \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P \quad \dots \text{ (IV.22)}
 \end{aligned}$$

For a gm-mole of an ideal gas, where $\left(\frac{\partial U}{\partial V} \right)_T = 0$,

$$\begin{aligned}
 C_P - C_V &= \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P \\
 &= P \left(\frac{\partial V}{\partial T} \right)_P = P \times \frac{R}{P} = R \quad \dots \text{ (IV.23)}
 \end{aligned}$$

The same result was obtained from considerations of the kinetic theory. The heat-content H and the internal energy U of an ideal gas, we have seen, are independent of pressure and volume. Since,

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \text{ and } C_V = \left(\frac{\partial U}{\partial T} \right)_V,$$

for an ideal gas both C_P and C_V would depend only on the temperature. From thermodynamics alone, a correlation between the heat-capacity and temperature cannot be derived. Usually both C_P and C_V increase with temperature. The commonly used empirical relations are

$$C_P = a + bT + cT^2 + \dots \quad \dots \text{ (IV.24)}$$

$$\text{and } C_V = a_1 + b_1 T \quad \dots \text{ (IV.25)}$$

$$\text{i.e., } \frac{dC_V}{dT} = \left(\frac{d^2 U}{dT^2} \right)_V = b_1$$

[where $a, b, c \dots$ and $a_1, b_1 \dots$ etc. are constants].

IV.13. Kirchhoff's Equation. If a system undergoes a change from a given state to another given state, both the internal energy and heat-content would alter. We may write

$$U_f - U_i = \Delta U$$

$$H_f - H_i = \Delta H$$

the suffixes f and i denote final and initial states.

Differentiating these with respect to temperature, at constant volume for the former and at constant pressure for the latter, we have,

$$\left[\frac{\partial(\Delta U)}{\partial T} \right]_V = \left[\frac{\partial U_f}{\partial T} \right]_V - \left[\frac{\partial U_i}{\partial T} \right]_V = C_{V_f} - C_{V_i} = \Delta C_V$$

$$\text{and } \left[\frac{\partial(\Delta H)}{\partial T} \right]_P = \left[\frac{\partial H_f}{\partial T} \right]_P - \left[\frac{\partial H_i}{\partial T} \right]_P = C_{P_f} - C_{P_i} = \Delta C_P$$

$$\text{or } \int \partial(\Delta U) = \int \Delta C_V dT$$

$$\text{and } \int \partial(\Delta H) = \int \Delta C_P dT$$

Integrating between the limits T° and 0° Abs., we find,

$$\Delta U - \Delta U_0 = \int_0^T \Delta C_V dT \quad \dots (IV.26)$$

$$\Delta H - \Delta H_0 = \int_0^T \Delta C_P dT \quad \dots (IV.27)$$

These relations are termed Kirchhoff's equations which enable us to find out the variations of internal energy-changes or heat-content changes with temperature, from thermal data. The relations would apply to all changes, physical or chemical. It is necessary to remember that ΔC_V and ΔC_P are the differences of the heat-capacities of the system at the final and initial states.

Most of the physical and chemical changes are often carried out under constant pressure and equation (IV.27) is commonly employed. We see by applying equation (IV.24),

$$\begin{aligned} \Delta H_T - \Delta H_0 &= \int_0^T \Delta C_P dT = \int_0^T (C_{Pf} - C_{Pi}) dT \\ &= \int_0^T (a_f + b_f T + c_f T^2 \dots - a_i - b_i T - c_i T^2 \dots) dT \\ &= \int_0^T (a + \beta T + \gamma T^2 + \dots) dT \\ &= aT + \frac{\beta T^2}{2} + \frac{\gamma T^3}{3} + \dots \quad \dots (IV.28) \end{aligned}$$

where

$$a = a_f - a_i, \beta = b_f - b_i, \text{ etc.}$$

A useful application of such relations is illustrated in the problem given below.

Problem : The heat of formation of ammonia from its elements is 11030 calories per mole at 27°C . What will be its heat of formation at 1000°C ? Given

$$C_{P(\text{H}_2)} = 6.94 - 0.2 \times 10^{-3}T; C_{P(\text{N}_2)} = 6.45 + 1.4 \times 10^{-3}T$$

and

$$C_{P(\text{NH}_3)} = 6.2 + 7.8 \times 10^{-3}T - 7.2 \times 10^{-6}T^2$$

The reaction is, $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 = \text{NH}_3$ ($\Delta H_{300} = -11030$ cal.)

$$\text{By equation (IV.24), } \Delta H_T - \Delta H_0 = \int_0^T \Delta C_P dT$$

$$= \int_0^T \left[C_{P(\text{NH}_3)} - \frac{1}{2}C_{P(\text{H}_2)} - \frac{3}{2}C_{P(\text{N}_2)} \right] dT.$$

Now

$$C_{P(\text{NH}_3)} = 6.2 + 7.8 \times 10^{-3}T - 7.2 \times 10^{-6}T^2$$

$$\frac{3}{2}C_{P(\text{H}_2)} = 10.41 - 0.3 \times 10^{-3}T$$

$$\frac{1}{2}C_{P(\text{N}_2)} = 3.225 + 0.7 \times 10^{-3}T$$

$$\Delta C_P = -7.435 + 7.4 \times 10^{-3}T - 7.2 \times 10^{-6}T^2$$

$$\begin{aligned} \Delta H_T &= \Delta H_0 + \int_0^T (-7.435 + 7.4 \times 10^{-3}T - 7.2 \times 10^{-6}T^2) dT \\ &= \Delta H_0 - 7.435T + 3.7 \times 10^{-3}T^2 - 2.4 \times 10^{-6}T^3 \end{aligned}$$

$$\therefore \Delta H_{T'} = \Delta H_0 - 7.435T' + 3.7 \times 10^{-3}T'^2 - 2.4 \times 10^{-6}T'^3$$

$$\begin{aligned} \text{So } \Delta H_{1273} - \Delta H_{300} &= -7.435(1273-300) + 3.7 \times 10^{-3}(1273^2-300^2) - 2.4 \times 10^{-6} \\ &\quad \times (1273^3-300^3) \\ &= -1091 \text{ cal.} \end{aligned}$$

$$\therefore \Delta H_{1273} = \Delta H_{300} - 1091 = -11030 - 1091 = -12121 \text{ calories.}$$

IV.14. Adiabatic Processes. The adiabatic changes of a system do not permit any heat-transfer between itself and the surroundings *i.e.*, $dQ = 0$. Hence, from the 1st Law,

$$dU + dW = dQ = 0 ; \text{ or } dU = -dW$$

Any work done on the system will increase the internal energy and conversely, the decrease in internal energy in such a process will be equal to the work done by the system. If the system suffers only mechanical expansion or contraction, then for minute change of the system under a pressure P , we have

$$dU = -dW = -PdV \quad \dots \text{ (IV.29)}$$

In a system containing ideal gases, we know, $dU = C_V dT$. Hence, for ideal gases,

$$C_V dT = -PdV \quad \dots \text{ (IV.30)}$$

$$\text{or } C_V dT = -\frac{RT}{V} dV \text{ (for one gm-mole)}$$

$$\text{or } C_V \frac{dT}{T} = -R \frac{dV}{V}$$

$$\text{or } C_V d \ln T = -R d \ln V$$

$$\text{or } C_V \ln T = -R \ln V + z \text{ (constant)}$$

If the initial and final temperatures of the ideal-gas system be T_1 and T_2 and volumes V_1 and V_2 respectively,

$$C_V \ln \frac{T_1}{T_2} = -R \ln \frac{V_1}{V_2}$$

$$\text{or } \ln \frac{T_1}{T_2} = \ln \left(\frac{V_2}{V_1} \right)^{\frac{R}{C_V}}$$

$$\text{from equation (IV.23), } \ln \frac{T_1}{T_2} = \ln \left(\frac{V_2}{V_1} \right)^{\frac{C_P - C_V}{C_V}} = \ln \left(\frac{V_2}{V_1} \right)^{\gamma - 1}$$

where $\gamma = \frac{C_P}{C_V}$, ratio of heat-capacities at constant pressure and at constant volume.

$$\text{Hence, } T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} = \text{constant}$$

Substituting T by $\frac{PV}{R}$ in this relation,

$$\frac{P_1 V_1}{R} V_1^{\gamma-1} = \frac{P_2 V_2}{R} V_2^{\gamma-1} = \text{constant}$$

$$\text{or } P_1 V_1^\gamma = P_2 V_2^\gamma = \text{constant}$$

$$\text{Similarly, } P_1 \left(\frac{RT_1}{P_1} \right)^\gamma = P_2 \left(\frac{RT_2}{P_2} \right)^\gamma = \text{constant}$$

$$\text{or } T_1^\gamma P_1^{1-\gamma} = T_2^\gamma P_2^{1-\gamma} = \text{constant}$$

$$\text{or } T_1 P_1^{\frac{1-\gamma}{\gamma}} = T_2 P_2^{\frac{1-\gamma}{\gamma}} = \text{constant}$$

In an adiabatic mechanical change of an ideal gas, then

$$PV^\gamma = \text{constant}, TV^{\gamma-1} = \text{constant}, TP^{\frac{1-\gamma}{\gamma}} = \text{constant} \quad \dots (IV.31)$$

In an isothermal change $PV = \text{constant}$, while in an adiabatic change $PV^\gamma = \text{constant}$, where $\gamma > 1$. Hence if the given pressure of a gas be reduced to the same extent isothermally and also adiabatically separately, then the final volume in the adiabatic process would be less than that in the isothermal process. The adiabatic indicator diagram has therefore a greater slope than that of the isothermal. We shall find such cases in dealing with cyclic processes later on.

Adiabatic Work. We have just seen that the adiabatic work done by a system is, (IV.29),

$$\Delta W = -\Delta U = P\Delta V. \text{ Since } \Delta U = C_V dT, \quad \dots (IV.32)$$

the adiabatic work, $\Delta W = -\Delta U = -C_V dT = C_V(T_1 - T_2)$ where T_1 and T_2 are the initial and final temperatures of the system. For 1 mole of ideal gas, $T = PV/R$. Hence substituting this in eqn. (IV.32), we obtain for system of ideal gases, adiabatic work,

$$\begin{aligned} \Delta W &= C_V \left(\frac{P_1 V_1}{R} - \frac{P_2 V_2}{R} \right) = \frac{P_1 V_1 - P_2 V_2}{R/C_V} \\ &= \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} \quad \dots (IV.33) \end{aligned}$$

where P_1 and V_1 are the initial pressure and volume and P_2, V_2 are the final pressure and volume.

Problem : Five litres of a monatomic gas expand adiabatically from five atmospheres to one atmosphere. The final volume is 11.8 litres. Calculate the adiabatic work.

$$\text{From (eqn. IV.32),} \quad W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

$$\text{Hence} \quad W = \frac{5 \times 5 - 1 \times 11.8}{1.66 - 1} = 20 \text{ litre-atmospheres.}$$

(The gas is monatomic, therefore $\gamma = 1.66$)

Problem : 70 gms of nitrogen gas was initially at 50 atm. and 25°C .

(a) It was allowed to expand isothermally against a constant external pressure of one atmosphere. Calculate ΔU , ΔH , ΔQ and ΔW , assuming the gas to behave ideally.

(b) Also find out the maximum work that would be obtained if the gas expanded reversibly and isothermally to one atmosphere.

$$(a) \text{ Amount of gas, } n = \frac{70}{28} = 2.5 \text{ gm-moles.}$$

Initial pressure, $P_1 = 50 \text{ atm}$; final pressure $P_2 = 1 \text{ atm}$.

Since the gas is ideal, $\Delta U = 0$ and also $\Delta H = 0$, as the temp. is constant.

$$\begin{aligned} \text{The work obtained } \Delta W &= P_2(v_2 - v_1) = P_2 \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right) = \frac{nRT \cdot P_2 \cdot (P_1 - P_2)}{P_1 P_2} \\ &= \frac{2.5 \times 2 \times 298 \times 1 \times (50 - 1)}{50 \times 1} \text{ calories} \\ &= 1.5 \text{ Kcals.} \end{aligned}$$

Since $\Delta W = \Delta Q$, $\therefore \Delta Q = 1.5 \text{ kcals.}$

(b) The maximum work for its isothermal reversible expansion,

$$\Delta W = nRT \ln \frac{P_1}{P_2} = 2.5 \times 2 \times 298 \times 2.303 \log \frac{50}{1} = 5.8 \text{ Kcals.}$$

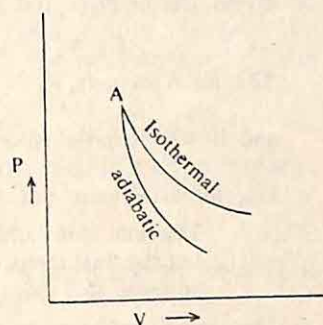


FIG IV.9

Problem : 100 gm of nitrogen gas initially at 25°C and 10 atm expands adiabatically against constant pressure of one atmosphere. Assume the gas to be ideal and its heat capacity $C_P = 6.96$ cal/mole. Calculate the final temperature, and ΔU and ΔH .

Given 100 gm $N_2 = 100/28 = 25/7$ gm.-moles, and

$C_P = 6.96$, i.e., $C_V = 4.96$, as the gas is ideal.

The initial pressure, $P_1 = 10$ atm. ; initial temp = 298°K,

and hence the initial volume $V_1 = \frac{nRT_1}{P_1} = \frac{25}{7} \times \frac{.081 \times 298}{10} = 8.67$ litres

i.e., initial volume per gm-mole, $v_1 = 2.44$ litres.

The final (constant) pressure $P_2 = 1$ atm.

Let the final temperature be T_2 and the volume V_2 .

Suppose also that final volume per mole = v_2 .

Then in adiabatic expansion of 1 gm-mole of the gas against constant pressure $P_2 (= 1 \text{ atm.})$, we have

$$C_V dT = -P_2 dv = -P_2(v_2 - v_1) = P_2(v_1 - v_2)$$

$$\text{or } 4.96 (T_2 - T_1) = 1(2.44 - v_2) \times 24.2 \text{ cal.}$$

[1 lit-atm = 24.2 cal]

$$\text{Again } \frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}, \text{ or } \frac{v_2}{T_2} = \frac{P_1 v_1}{P_2 \times T_1} = \frac{10 \times 2.44}{298} = \frac{24.4}{298}$$

$$\text{or } v_2 = \frac{24.4}{298} T_2$$

$$\text{Substituting, } 4.96 (T_2 - 298) = \left(2.44 - \frac{24.4}{298} T_2 \right) 24.2$$

$$\text{whence } T_2 = 222^\circ \text{K.}$$

$$\therefore v_2 = \frac{24.4}{298} \times 222 \text{ per mole.}$$

$$\text{The final volume of the given sample, } V_2 = \frac{25}{7} \times \frac{24.4 \times 222}{298} = 64.3 \text{ litres.}$$

$$\text{Now } \Delta U = -nc_V dT$$

$$= -\frac{25}{7} \times 4.96 \times (298 - 222) = -1346 \text{ cal.}$$

$$\text{And } \Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2 V_2 - P_1 V_1)$$

$$= -1346 + (1 \times 64.3 - 10 \times 8.67) \times 24.2$$

$$= -1888 \text{ cal.}$$

THERMOCHEMISTRY

Chemical reactions are always associated with heat-changes. Those reactions in which heat energy escapes from the system to the surroundings are termed *exothermic* reactions, while the chemical processes where heat is absorbed by the system from the surroundings are called *endothermic* reactions. The quantities of heat evolved or absorbed in a chemical process certainly depend on the way the change is carried out, i.e., on the path. Thus, when zinc and mercury sulphate solution react freely in a beaker, considerable amount of heat would be evolved but when the same reaction is carried out in Clarke's voltaic arrangement, heat evolution is less and a large portion of the energy is available as electric work. It is therefore necessary to mention the mode of chemical reaction while specifying the heat-change in a chemical process.

IV.15. Heat Changes at Constant Pressure and at Constant Volume. Most of the reactions occur under atmospheric pressure or under some constant pressure.

The homogeneous reactions in solution or reactions in a closed vessel take place at constant volume. As such, the reactions are studied usually under two specified conditions either at constant pressure or at constant volume.

If the reaction takes place at constant pressure the heat-changes may be expressed as Q_P , and similarly the heat-change at constant volume is Q_V . We know, heat-change at constant pressure is the change in the heat-content of the system,

$$Q_P = \Delta H_P = H_{\text{resultant}} - H_{\text{reactants}}$$

Assuming that during the process, work performed, if any, would be mechanical, we can write,

$$Q_P = \Delta H_P = \Delta U_P + P\Delta V \quad \dots (IV.34)$$

ΔV , being the change in the volume of the system in the chemical process. The suffix P denotes that pressure is being maintained constant.

On the other hand, if the chemical process takes place at constant volume, there is no mechanical work.

$$\text{Hence,} \quad Q_V = \Delta U_V \quad \dots (IV.35)$$

Subtracting (IV.35) from (IV.34).

$$Q_P - Q_V = \Delta U_P - \Delta U_V + P\Delta V$$

It cannot be presumed that ΔU_P would be equal to ΔU_V for a given process. In gaseous reactions, the components are often supposed to behave ideally, and in such a case, the energy-contents are independent of pressure or volume, so that ΔU_P and ΔU_V are the same. In other chemical reactions, ΔU_P and ΔU_V differ only to a very little extent and the difference is negligible compared to the large heat-effects. So it is usually assumed, $\Delta U_P = \Delta U_V$

$$\text{Hence,} \quad Q_P = Q_V + P\Delta V \quad \dots (IV.36)$$

In a gaseous reaction if n_1 moles of reactants are transformed into n_2 moles of resultants, then the increase in the number of gm-molecules due to the reaction is $(n_2 - n_1)$. If V denotes the volume of a gm-molecule at the temperature and pressure of the reaction, the volume-change in the chemical process,

$$\Delta V = (n_2 - n_1)V = \Delta n \frac{RT}{P}$$

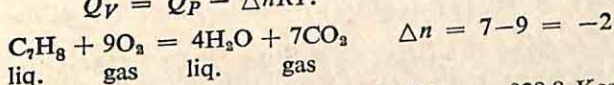
Substituting in equation (IV.36),

$$Q_P = Q_V + P\Delta V = Q_V + \Delta n RT. \quad \dots (IV.37)$$

where Δn is the increase in the number of moles in the chemical reaction.

The heat of combustion of liquid toluene to carbon dioxide and liquid water is -930 Kcals. at constant pressure. Calculate the heat of its combustion at constant volume at 27°C .

$$Q_V = Q_P - \Delta n RT.$$

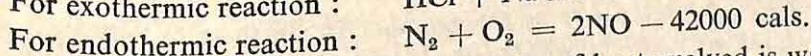
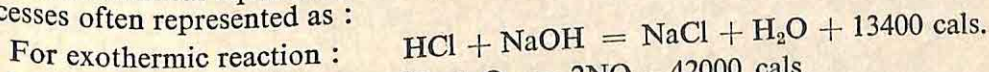


Hence

$$Q_V = -930 - (-2)(2 \times 10^{-3}) \times 300 = -928.8 \text{ Kcals.}$$

(Volumes of liquids are comparatively negligible.)

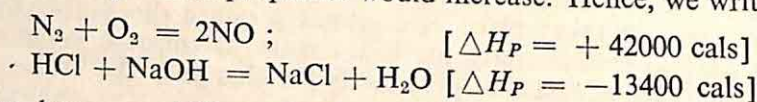
IV.16. Notations. The modes of expression of heat-changes for chemical processes are somewhat different in texts of chemistry and thermodynamics. In chemistry, the thermochemical equations, *i.e.*, equations showing energy-changes in chemical processes often represented as :



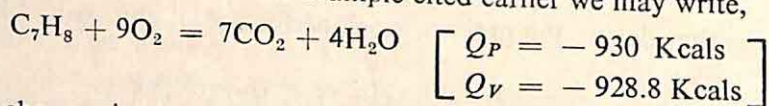
That is, in case of heat-evolution, the quantity of heat evolved is written with the products with a positive sign. In heat absorption, the quantity of heat is written with the resultants with a negative sign.

$$\text{Hence,} \quad 13400 \text{ cal} = H_{(\text{HCl} + \text{NaOH})} - H_{(\text{NaCl} + \text{H}_2\text{O})}$$

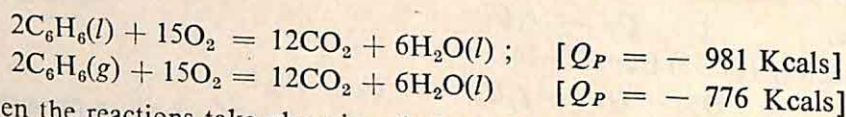
In thermodynamics, the attention is concentrated on the system as a whole. In exothermic changes, heat-content or energy-content of the system would diminish. In endothermic changes these properties would increase. Hence, we write,



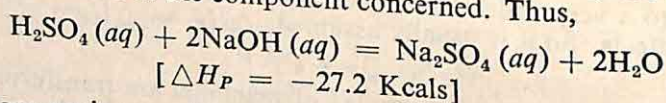
In these cases, however, ΔH_P and ΔU_V i.e., Q_P and Q_V would be equal, as there is no volume-change involved. In the example cited earlier we may write,



The heat-changes in chemical reactions also depend upon the physical state of the reactants and resultants. To indicate the physical state, gas, liquid and solid are represented by letters, *g*, *l* and *s* on the side of their formulae. To illustrate, the heats produced in the oxidation of liquid and gaseous benzene are expressed as follows :



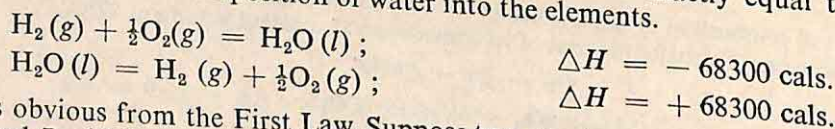
When the reactions take place in solution, the heats of reaction depend to some extent on the concentration of the solutions. In very dilute solutions, the heats of reaction attain a constant value. Such solutions will not undergo any heat-change on further dilution. To express such a state of dilution, the symbol (*aq*) is often written on the side of the component concerned. Thus,



means the solutions are in very dilute state and no heat-change is caused by further dilution during the process.

IV.17. The Laws of Thermochemistry. The thermal changes in chemical processes are governed by two general principles, both of which are, of course, corollaries of the First Law.

A. Law of Lavoisier and Laplace. This law states that *the heat-change accompanying a chemical process in one direction is equal in magnitude but opposite in sign, to that accompanying the same reaction in the reverse direction.* That is, heat evolved when water is formed from hydrogen and oxygen is exactly equal to the heat absorbed in the decomposition of water into the elements.



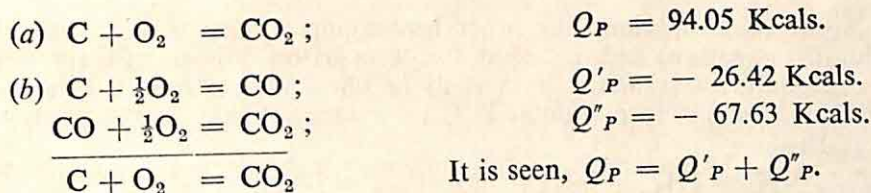
It is obvious from the First Law. Suppose two reactants *A* and *B* change first into *C* and *D* with heat evolution (Q) and subsequently *C* and *D* react to produce back *A* and *B* in the initial state with heat absorbed (Q'). According to the First Law, heat-content (H) or energy-content (U) of the initial *A* and *B* would again return to the same magnitude. As such the net heat-content change or energy-content change would be zero. Hence,

$$Q + Q' = 0 ; \quad \text{or, } Q = -Q'$$

i.e., heat-changes in the two directions must be equal in magnitude but opposite in sign.

B. Hess's Law of Constant Heat Summation. This law states that *for a given chemical process, the net heat-change (Q_P or Q_V) will be the same whether the process occurs in one or in several stages.*

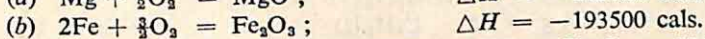
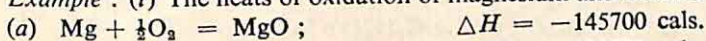
To illustrate, carbon and oxygen can give directly carbon dioxide, or these can first form carbon monoxide which may then be oxidised to carbon dioxide. The net heat-changes in the two paths are equal.



In accordance with the First Law, if the initial and final states be fixed, the change in the heat content or energy content of a system *i.e.*, ΔH_P and ΔU_V would be independent of the path. Hence Q_P and Q_V will be independent of the path, *i.e.*, heat-change of a reaction will be the same whether the reaction takes place in a single step or in several steps.

One singular advantage of this principle is that we can add or subtract the heat-changes in the process, as we have seen in the example of carbon dioxide formation just now. In other words, the thermochemical equations may be treated algebraically. Some examples are given below.

Example : (i) The heats of oxidation of magnesium and iron are given :

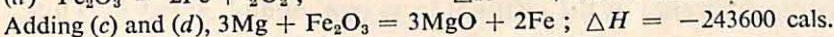


Calculate the heat produced in the reaction : $3\text{Mg} + \text{Fe}_2\text{O}_3 = 3\text{MgO} + 2\text{Fe}$.

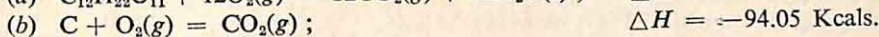
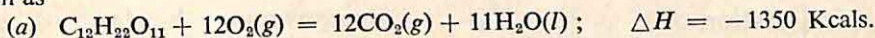
Multiplying (a) by 3,



and reversing (b),

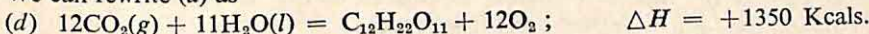


Example : (ii) The heats produced in the oxidation of cane sugar, carbon and hydrogen are given as

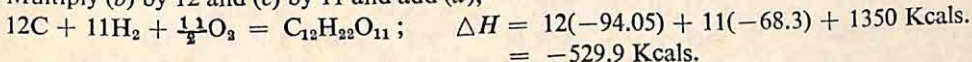


Calculate the heat produced if the canesugar were produced directly from the elements.

We can rewrite (a) as



Multiply (b) by 12 and (c) by 11 and add (d),



Hence, by applying Hess's law we can calculate the heat of a reaction in the formation of a compound though the elements would not directly combine to produce the compound.

These examples clearly illustrate the utility of the law of heat summation.

IV.18. Types of Heat Changes. The heat-changes involved in different transformations have been given different names depending upon the nature of the processes, such as heat of formation, heat of combustion, heat of dilution, etc.

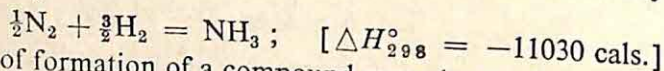
A. Heat of Formation. It is defined as the amount of heat-change that occurs when a gm-molecule of the substance is formed from the constituent elements. In the production of a mole of water from hydrogen and oxygen 68.9 kilo-calories of heat are evolved. Hence, the heat of formation of water is -68.9 Kcals.



Thus " -96960 calories is the heat of formation of carbon dioxide" means that when, 1 gm-mole of CO_2 is obtained from carbon and oxygen, the heat evolved would be 96960 calories.

If heat is evolved during the formation of the compound from its elements, the compound is an *exothermic* one. On the other hand, if heat is absorbed in the formation of a compound, as in nitric oxide, the compound is called, *endothermic*.

The heats of formation, like other heat-changes, vary with temperature (cf. Kirchhoff's equation) and therefore, for comparison of heats of formation of different compounds a standard state is to be chosen. It is now customary to express standard heats of formation at 25°C ; the standard heat may be symbolised as ΔH°_{298} . Thus,

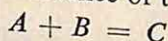


The heat of formation of a compound may also be determined from a knowledge of the heat-capacities by the application of Kirchhoff's equation.

TABLE : STANDARD HEATS OF FORMATION AT 25°C IN KCALS

Compound	ΔH°_{298}	Compound	ΔH°_{298}
H ₂ O (l)	- 68.32	NaCl (s)	- 98.3
CO (g)	- 26.42	KCl (s)	-104.3
CO ₂ (g)	- 94.05	CH ₄ (g)	- 17.9
SO ₂ (g)	- 70.9	C ₂ H ₆ (g)	- 20.2
N ₂ O (g)	+ 19.7	C ₂ H ₄ (g)	+ 12.5
NO (g)	+ 21.6	C ₂ H ₂ (g)	+ 54.2
H ₂ S (g)	- 5.3	C ₆ H ₆ (l)	+ 11.7
HCl (g)	- 22.06	CH ₃ OH (l)	- 57.0
NaOH (s)	-102.0	C ₂ H ₅ OH (l)	- 66.4
KOH (s)	-102.0	HNO ₃ (l)	- 42.0

If a compound C is produced from the elements A and B then the heat of formation of C is the difference of the heat-contents of C and of A and B. Thus,

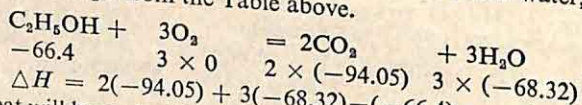


$$H_A H_B H_C \text{ (heat contents)}$$

Then heat of formation of C = $H_C - H_A - H_B$. By convention the standard heat-contents of all elements are taken as zero, i.e., $H_A = H_B = \dots = 0$.

Then the heat content of the compound C = heat of formation of C. This procedure would prove very helpful in determining the heats of reactions.

Example : Calculate the heat of oxidation of ethanol to CO₂ and water, taking heats of formation of ethanol, CO₂ and H₂O from the Table above.



$$\Delta H = 2(-94.05) + 3(-68.32) - (-66.4) = -326.6 \text{ Kcals.}$$

That is, 326.6 Kcals of heat will be evolved in the oxidation of ethanol.

B. Heat of Combustion. The heat-change associated with the complete combustion of a gm-mole of the substance at a given temperature under normal pressure is called its heat of combustion.

We have seen that 68.9 Kcals. is the heat of formation of water. It may also be called heat of combustion of hydrogen. In the example just cited the heat of oxidation of ethanol is 326.6 Kcals. In reality, it is heat of combustion of ethanol which has suffered complete combustion. Usually in the case of organic compounds complete combustion is regarded to have taken place when these are burnt finally to carbon dioxide and water. A few data of heats of combustion are given below.

TABLE : HEATS OF COMBUSTION AT 25°C IN KCALS

Compounds	ΔH	Compounds	ΔH
Methane	- 212.8	Methanol (l)	- 173.6
Ethane	- 372.8	Ethanol (l)	- 326.7
Ethylene	- 337.2	Cane sugar (s)	-1349.0
Acetylene	- 310.6	Phenol (s)	- 732.0
Benzene (l)	- 780.9	Aniline (l)	- 812.0
Naphthalene (s)	-1228.2	Benzoic acid (s)	- 771.4

The heat of combustion is usually determined in a 'bomb calorimeter' made of steel, internally enamelled with platinum (Fig. IV.10). It has a capacity of about 400 c.c. and is fitted with pressure-tight screw-cap. A weighed sample is placed in a cup inside and the bomb is filled with oxygen at 30 atm. pressure. The reaction is started by heating electrically a thin wire dipped into the sample. The reaction, once started, proceeds rapidly with evolution of a large amount of heat. The bomb is kept immersed in water and the amount of heat evolved is determined from temperature-rise. The heat-capacity of the system is predetermined by the electrical method or by burning a standard substance (say benzoic acid) of known heat of combustion. It is, of course, necessary to insulate the bomb and the water from the surroundings very carefully. The method gives result up to an accuracy of 0.01 percent. The heats of formation or heats of other reactions can be evaluated from the heat of combustion.

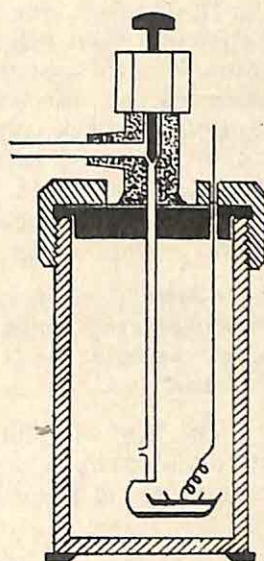


FIG. IV.10

Example : Calculate the heat of formation of ammonia. The heats of combustion of ammonia and hydrogen are 9.06 and 68.9 Kcals. respectively.

Given (1) $2\text{NH}_3 + 3\text{O} = \text{N}_2 + 3\text{H}_2\text{O}$; $\Delta H = -2 \times 9.06 = -18.12$

(2) $\text{H}_2 + \text{O} = \text{H}_2\text{O}$; $\Delta H = -68.9$

or (3) $3\text{H}_2 + 3\text{O} = 3\text{H}_2\text{O}$; $\Delta H = -3 \times 68.9$

Subtracting (3) from (1) and re-arranging

$$2\text{NH}_3 = \text{N}_2 + 3\text{H}_2 ; \quad \Delta H = -18.12 + 3 \times 68.9 = +188.58$$

i.e., (4) $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$; $\Delta H = -188.58$

Hence, heat of formation of ammonia, $\Delta H = -94.29$ Kcal.

Example : The heat of combustion of ethyl alcohol is 325100 calories and that of acetic acid is 209500 calories. Calculate the heat evolved in the reaction $\text{C}_2\text{H}_5\text{OH} + \text{O}_2 = \text{CH}_3\text{COOH} + \text{H}_2\text{O}$.
Given

(1) $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 = 2\text{CO}_2 + 3\text{H}_2\text{O}$; $\Delta H = -325100$

(2) $\text{CH}_3\text{COOH} + 2\text{O}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O}$; $\Delta H = -209500$

Subtracting (2) from (1) and re-arranging :

$$\text{C}_2\text{H}_5\text{OH} + \text{O}_2 = \text{CH}_3\text{COOH} + \text{H}_2\text{O} ; \Delta H = -325100 + 209500 = -115600 \text{ cal.}$$

i.e., the heat of reaction is -115600 cal.

C. Heat of Transition. When a substance changes from one modification into another, such as α -sulphur into β -sulphur, the transformation is also accompanied with heat-change, which is termed *heat of transition*. The heat of transition (as well as the latent heat) really is the measure of the difference in heat-contents of the two forms of matter at the temperature of the transition.

The heats of transition can be ascertained from observation of the heat of reaction when the two forms of the substance are made to undergo separately the same type of a chemical change. Thus, the heats of oxidation of diamond and graphite are :



By subtraction ; $\text{C}_{(\text{dia})} - \text{C}_{(\text{gra})} = 450 \text{ cal.}$

or $\text{C}_{(\text{diamond})} = \text{C}_{(\text{graphite})} ; (\Delta H = -450 \text{ cal.})$

Obviously, the heat-content of graphite is less than that of the diamond.

D. Heat of Solution and Heat of Dilution. Generally speaking, the net heat-change that takes place when a gm-mole of the solute is completely dissolved in a solvent is called the heat of solution or, more appropriately, *integral heat of solution*. When a solute dissolves, it is *ipso facto* in a molten state and as such the heat of solution should be equivalent to the latent heat of fusion of a solid. In the case of gaseous solutes, it would be equal to the latent heat of sublimation. If the latent heat were equal to the heat of solution, the solution must be regarded as an *ideal* one. But these two quantities, latent heat and heat of solution, are different due to interaction between the solutes and the solvent.

In overwhelming number of cases, we deal with aqueous solutions. With gaseous solutes, usually the heat of solution is negative (*i.e.*, exothermic). When solid solutes are dissolved in water, the heat of solution may be negative or positive. The hydrated salts very often have positive heats of solution.

The heat of solution however changes with concentration. One gm-mole of KCl dissolved in 50 moles of water and 200 moles of water will cause different heat-changes, as the Table below would illustrate :

TABLE : HEATS OF SOLUTION AT 25°C IN CALORIES

Solute : KCl		Solute : HCl	
moles of water per mole of KCl	ΔH	moles of water per moles of HCl	ΔH
12	+ 3786	50	- 17400
50	+ 4276	100	- 17540
100	+ 4391	200	- 17630
200	+ 4449	400	- 17710
∞	+ 4404	∞	- 17880

The value of the heat of solution, obtained graphically by extrapolating ΔH to infinite dilution is called the integral heat of solution at infinite dilution. In fact, when the solution becomes very dilute, the heat-change assumes a constant value, as shown in Fig. (IV.11) for KCl solutions.

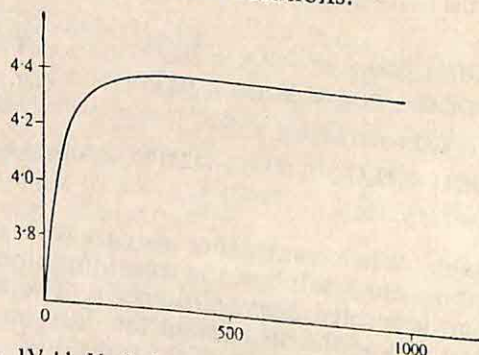


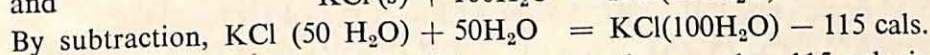
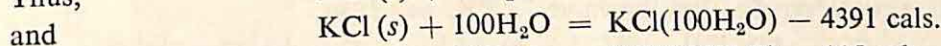
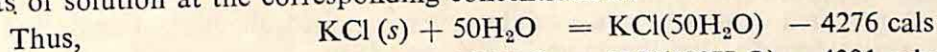
FIG. IV.11 Variation of heat of solution with dilution

[ΔH in Kcals. is plotted against moles of water n_1 , n_1 plotted along horizontal axis.]

It is obvious that during the process of dissolution of a gm-mole of solute, the concentration continuously changes and hence the magnitude of heat changes would also vary. The heat of solution at any instant, $\Delta H/\Delta n$, is called the *differential heat of solution*. This is indeed a partial molal quantity.

Since the heat of solution varies with concentration the addition of a quantity of solvent to a given solution of fairly high concentration would involve a thermal change. The net heat-change associated with the dilution of a solution containing

1 mole of solute from a concentration C_1 to a concentration C_2 is called the *integral heat of dilution*. These integral heats of dilution are evidently the differences of the heats of solution at the corresponding concentrations.



i.e., in diluting $\text{KCl}(50\text{H}_2\text{O})$ to half its concentration another 115 calories of heat would be absorbed.

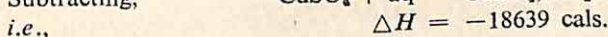
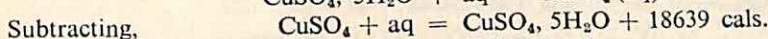
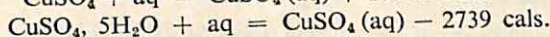
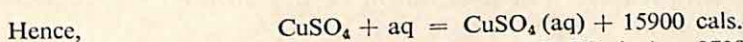
Problem : 100 gms. of anhydrous CuSO_4 , when dissolved in excess of water produced 10,000 calories of heat. The same amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ on dissolving in large excess of water absorbed 1,100 calories. What is the heat of hydration of CuSO_4 ?

$$100 \text{ gms. CuSO}_4 = \frac{100}{159} \text{ gm-mole.}$$

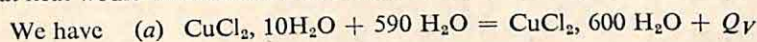
$$\therefore \text{heat of solution of CuSO}_4 = - \frac{10000 \times 159}{100} = -15900 \text{ cal.}$$

$$100 \text{ gms. of CuSO}_4 \cdot 5\text{H}_2\text{O} = \frac{100}{249} \text{ gm. moles.}$$

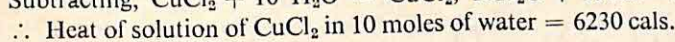
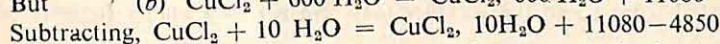
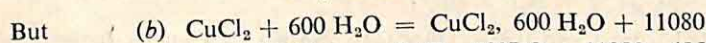
$$\therefore \text{heat of solution of CuSO}_4 \cdot 5\text{H}_2\text{O} = 1100 \times \frac{249}{100} = +2739 \text{ cal.}$$



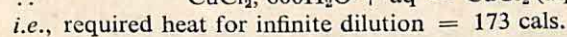
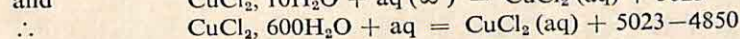
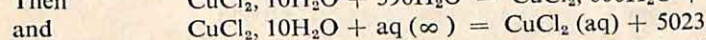
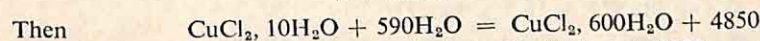
Problem : A solution of composition $\text{CuCl}_2 + 10\text{H}_2\text{O}$ is diluted with x moles of water, the heat disengaged is given by $Q_V = \frac{x \times 5023}{x + 21.24}$. The heat of solution of CuCl_2 in 600 moles of water is 11080 calories. Find out the heat of solution of anhydrous CuCl_2 in 10 moles of water. What heat would be evolved if a solution $\text{CuCl}_2 + 600 \text{H}_2\text{O}$ be infinitely diluted?



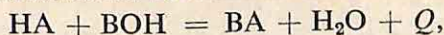
where, $Q_V = \frac{x \times 5023}{x + 21.24} = \frac{590 \times 5023}{590 + 21.24} = 4850 \text{ cal.}$



Again, if $x = \infty$, $Q_\infty = \frac{x \times 5023}{x + 21.24} = \frac{x \times 5023}{x} = 5023 \text{ cal.}$

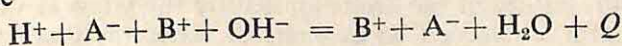


E. Heat of Neutralisation. The amount of heat liberated when one gm-equivalent of an acid just neutralises one gm-equivalent of a base in dilute solutions, is called the heat of neutralisation. If the acid HA neutralises the base BOH , then



where Q is the heat of neutralisation.

If the acid and the base are both strong, complete dissociation may be assumed, and we can write



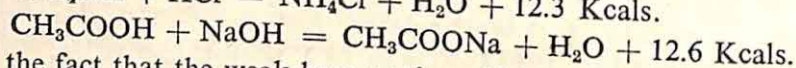
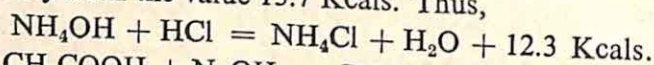
or,



Hence, the heat of neutralisation is really the heat of formation of a gm-mole of

water from a gm-ion of hydrogen and a gm-ion of hydroxyl ions. This is corroborated from the fact that heat of neutralisation between any strong acid and any strong base is always the same and equal to 13.7 Kcals.

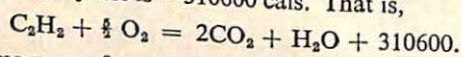
But when a weak acid or a weak base is neutralised, the heat of neutralisation differs considerably from the value 13.7 Kcals. Thus,



This is due to the fact that the weak base or the acid is very slightly dissociated and a portion of the energy is utilised in the process of dissociation of the weak counterpart as the reaction proceeds.

IV.19. Heat of Reaction and Flame Temperatures. If a spontaneous process takes place suddenly and the heat produced during the chemical process has no opportunity to be dissipated to the surroundings, obviously the heat will increase the temperature of the resultant system. It is a process practically equivalent to an adiabatic one. Such a condition does, in practice, arise in the production of flames. The gas or gases which undergo combustion produce a large quantity of heat which is mostly utilised in heating up the flame-zone containing the gases produced after combustion. If we know the heat of reaction and the composition and heat-capacities of the resultant gases, we can calculate easily to what temperature these gases can be raised by the heat of combustion in the flame. Thus, we can ascertain the maximum flame temperature. An illustration in the burning of acetylene in air would be a suitable one.

The heat of combustion of acetylene is -310600 cal. That is,



The gases present in the flame-zone after combustion are carbon dioxide, water vapour and the unreacted nitrogen of the air. Since $5/2$ moles of oxygen were required for combustion, nitrogen present would be approximately 10 moles. Hence the composition of the resultant gases would be 2 moles CO_2 , 1 mole H_2O vapour and 10 moles nitrogen. The heat-capacities of these gases approximately are,

$$2 \times C_{P\text{CO}_2} = 2(6.4 + 10.1 \times 10^{-3}T) = 12.8 + 20.2 \times 10^{-3}T$$

$$C_{P\text{H}_2\text{O}} = 7.22 + 2.4 \times 10^{-3}T$$

$$10 \times C_{P\text{N}_2} = 10(6.45 + 1.4 \times 10^{-3}T) = 64.5 + 14 \times 10^{-3}T$$

$$\therefore \Sigma \nu C_P = 84.52 + 36.6 \times 10^{-3}T$$

These gases have been heated from room temperature (say 298°K) to a higher temperature T by the heat of combustion.

$$\therefore Q = \int_{298}^T \Sigma \nu C_P dT = \int_{298}^T (84.52 + 36.6 \times 10^{-3}T) dT$$

$$= [84.52T + 18.3 \times 10^{-3}T^2]_{298}^T$$

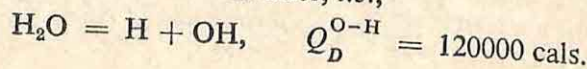
$$\text{i.e., } 84.52(T-298) + 18.3 \times 10^{-3}(T^2-298^2) = 310600$$

$$\text{or } 84.52T + 18.3 \times 10^{-3}(T^2) = 337415$$

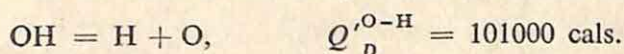
This gives the value of the maximum attainable temperature T approximately as 2450°K .

But the real flame temperature is somewhat less as some of the heat certainly radiates out. Moreover at the high temperature secondary reactions, like dissociation of water vapour or of carbon dioxide, do occur which have not been taken into consideration.

IV.20. Bond Energy and Dissociation Energy. The amount of energy required to separate an atom by breaking a bond with another atom in a given compound is called the 'dissociation energy' of that bond. This dissociation energy, say Q_D is dependent on the nature of the atoms united by the bond as well as the nature of the molecule as a whole. To be explicit, in water the dissociation energy of separating a H-atom will be 120000 calories, i.e.,



But when the second H-atom is separated from the residual OH group, a similar O—H bond is broken as before, but dissociation energy is different,



Similarly, the dissociation energy of C-H bond in methane and the same in benzene are different because the residual portions of the two molecules are different.

On the other hand, 'Bond energy' is the average value of the dissociation energies of a given bond in a series of different dissociating species. Thus in the above-noted example of water, the heat of dissociation of water into hydrogen and oxygen is 110000 cal, *i.e.*,

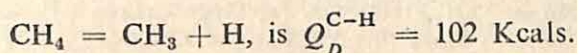


If we take the average of the dissociation energies of the two bonds of O—H in water, we have

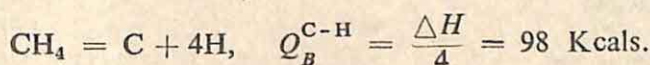
$$\frac{Q_D + Q'_D}{2} = \frac{120000 + 101000}{2} = 110500 \text{ cal,}$$

which is practically equal to the bond energy. Hence, bond energy Q_B is the average of the dissociating energy of the given bond in the whole species.

Let us take another example, that of methane. The dissociating energy of C-H bond as in



But the bond energy is somewhat different and is the mean value of the energies required to separate 4 successive atoms of hydrogen from the molecule. In fact,



where ΔH is the heat of the complete dissociation which involves breaking of four C—H bonds. In the case of diatomic molecules, however, the bond energy and the dissociation energy of a given bond must be the same.

In the calculation of thermal changes in chemical processes, the bond energies are useful and some of the accepted values are given here.

TABLE : BOND ENERGIES IN KCALS

Bond	Energy	Bond	Energy
C — C	83.1	H — H	103.2
C = C	140	O — O	33
C $\equiv$ C	198	O = O	118
C — H	99	Cl — Cl	57.8
C — O	84	Br — Br	46
C = O	173	I — I	36
C — Cl	78.5	N $\equiv$ N	225
C — N	69.7	O — H	110.5
N — H	93.4	Cl — H	103
C — Br	66	O — Cl	49

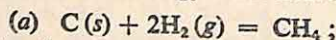
The *standard state* of an element is the state in which the element exists at 25°C and one atmosphere. The quantity of heat required to produce one mole of atoms in the gaseous atomic state from the element in the standard state is called the heat of atomisation of the element. The values of the heat of atomisation of a few elements are given here.

TABLE : HEAT OF ATOMISATION IN KCAJS

Element	Atomisation	ΔH Heat of atomisation (Kcals)
Carbon	$C(s) \rightarrow C(g)$ (graphite)	170.9
Hydrogen	$\frac{1}{2}H_2(g) \rightarrow H(g)$	52.1
Oxygen	$\frac{1}{2}O_2(g) \rightarrow O(g)$	59.6
Nitrogen	$\frac{1}{2}N_2(g) \rightarrow N(g)$	113.0
Chlorine	$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	28.9

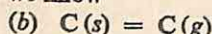
The knowledge of the heats of formation of a substance and the heats of atomisation of the constituents enables us to evaluate the bond-energy,

• **C—H bond energy** : The heat of formation of methane is -17.9 Kcals.

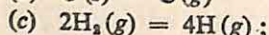


$$\Delta H_f = -17.9$$

and we know

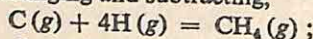


$$\Delta H = 170.9$$



$$\Delta H = 4 \times 52.1$$

Rearranging and subtracting,



$$Q = 17.9 + 170.9 + 4 \times 52.1$$

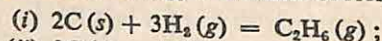
Q , net heat evolved.

$$= 397.2 \text{ Kcals.}$$

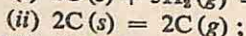
Conversely, in breaking the four C—H bonds, the energy required is 397.2 Kcals.

$$\therefore \text{C—H bond energy} = \frac{1}{4}(397.2) = 99.3 \text{ Kcals} \approx 99 \text{ Kcals.}$$

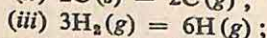
C—C bond energy : The heat of formation of ethane is -20.3 Kcals ; i.e.,



$$\Delta H_f = -20.3$$

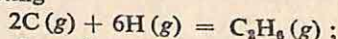


$$\Delta H = 2 \times 170.9$$



$$\Delta H = 6 \times 52.1$$

Rearranging and subtracting



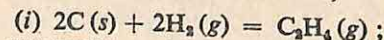
$$Q = 6 \times 52.1 + 2 \times 170.9 + 20.3 = 674.7$$

Hence, the necessary energy to break one C—C bond and 6 C—H bonds is 674.7 Kcals.

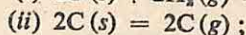
The bond energy of 6 C—H bonds = $6 \times 99 = 594$ Kcals.

$$\therefore \text{The C—C bond energy} = 674.7 - 594 = 80.7 \text{ Kcals.}$$

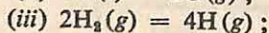
C=C bond energy : This is also obtained in a similar fashion. The heat of formation of ethylene is $+12.5$ Kcals. Therefore,



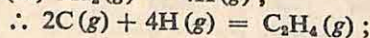
$$\Delta H_f = 12.5$$



$$\Delta H = 2 \times 170.9$$



$$\Delta H = 4 \times 52.1$$



$$Q = -12.5 + 2 \times 170.9$$

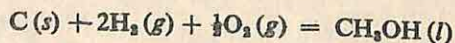
$$+ 4 \times 52.1 = 537.7.$$

The energy of 4 C—H bonds = $4 \times 99 = 396$

$$\therefore \text{C=C bond energy} = 537.7 - 396 = 141.7 \text{ Kcals.}$$

In such calculations it is presumed that the C—H bond energy in methane, ethane, ethylene etc. is the same. This is not strictly correct. The bond energy is subject to some variation due to environmental linkings. That is, the value of the bond energy depends upon the nature of the atoms linked with the neighbouring bonds and also to the stereochemistry of the molecule. The variation in the values is however often small.

Problem : Calculate the heat of formation of methyl alcohol from standard values of bond energies.



The energy changes are

Kcals

(i) atomisation of carbon (1 mole) = 170.9

(ii) atomisation of 2 moles hydrogen = 4×52.1

(iii) atomisation of $\frac{1}{2}$ mole oxygen = 59.6

(iv) formation of 3 C—H bonds	=	-3 × 99
(v) formation of 1 C—O bond	=	-84
(vi) formation of 1 O—H bond	=	-110.5
(vii) Liquefaction of 1 mole CH ₃ OH	=	-8.4

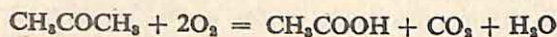
$$\text{Adding } \Delta H = -61.0 \text{ Kcals}$$

The heat of formation of the liquid alcohol is -61 Kcals.

If there exist one or more resonating structures in the substances considered, the resonance energy should also be taken into account. The resonance energy per mole in Kcals are given here.

Resonance energy (Kcals)						
Groups	→	C ₆ H ₆	Naph. C ₁₀ H ₈	COOH	CO ₂	COOEt
Res. energy	→	38	75	28	33	24

Problem : Calculate the heat of reaction in the following chemical process in the gaseous state :



The net bond energies (ϵ) for reactants and resultants are :

Reactants	Kcals	Resultants	Kcals
6 $\epsilon_{\text{C-H}}$	= 6 × 99	3 $\epsilon_{\text{C-H}}$	= 3 × 99
2 $\epsilon_{\text{C-C}}$	= 2 × 83.1	1 $\epsilon_{\text{C-C}}$	= 83.1
1 $\epsilon_{\text{C=O}}$	= 173	1 $\epsilon_{\text{C=O}}$	= 173
2 $\epsilon_{\text{O=O}}$	= 2 × 118	1 $\epsilon_{\text{O-H}}$	= 110.5
		2 $\epsilon_{\text{C=O}}$	= 2 × 173
		2 $\epsilon_{\text{O-H}}$	= 2 × 110.5
		Res. COOH	= 28
		Res. CO ₂	= 33
	1169.2		
			1301.6

$$\therefore \text{Heat of reaction} = -132.4 \text{ Kcals.}$$

THE SECOND LAW

IV.21. The need for the Second Law. The first law summarizes our experience regarding the transformation of energy. We have learnt that (i) the different forms of energy are interconvertible and (ii) when one form of energy disappears an equivalent amount of another kind must appear. But there is an element of incompleteness in the First Law. The First Law does not indicate whether the change would at all occur and, if it occurs, to what extent. Moreover, it also does not indicate the direction in which the process of transformation would take place.

To illustrate : (a) Suppose two bodies *A* and *B* are brought in contact. Then from the first law, we only know if *q* calories of heat are lost by *A*, exactly *q* calories of heat would be gained by *B*, or *vice-versa*. But the law does not state if *A* or *B* would lose the heat energy. To know the direction of flow of heat we need another information, namely, the temperatures of *A* and *B*.

(b) Again, consider the chemical change, $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$: the first law tells us only that if *z* calories of heat be evolved during the dissociation of pentachloride, then in the opposite reaction of combination of trichloride and chlorine exactly *z* calories of heat would be absorbed. But if we have an arbitrary mixture of PCl_5 , PCl_3 and Cl_2 , we cannot ascertain from the first law alone if there would be dissociation of pentachloride or not. To determine the direction in which the chemical change would occur, we require the knowledge of the equilibrium constant of the reaction.

(c) A copper and a zinc rod partially immersed in dilute sulphuric acid and externally connected will transform chemical energy to electrical energy. But whether the current will flow from copper to zinc or *vice versa* cannot be determined unless we are aware of the electrode potentials of the two metals.

These common examples show the insufficiency of the First Law. To ascertain the direction of a chemical or physical process we need some more information or the knowledge of some other criteria beyond the first law. The principle which would determine the direction as also the extent of a change is provided by the Second Law. Like the First Law, the Second Law is also truly a law of experience gathered from observations of nature. Any such experience which would determine the criteria for the direction for the occurrence of a change will be the basis of the Second Law. These experiences have been expressed in different ways by different workers. That is why we often find a large number of statements for the Second Law, though all of them lead to the same goal, namely to indicate the direction of a process.

IV.22. Spontaneous Processes. Changes taking place in a system without the aid of any external agency are termed *spontaneous processes*. We shall make an attempt here to collect experiences with some very simple spontaneous processes.

(i) Suppose a vessel containing a gas at higher pressure P_1 be connected by a tube to another vessel where the pressure is less, say P_2 , ($P_1 > P_2$). It is our experience that the gas would spontaneously move from the higher to the lower pressure. This process would continue until the two pressures are equalised and a *mechanical equilibrium* is established. Further we find that the change is unidirectional i.e., irreversible. When equilibrium is attained, the gas by itself will not rush back to the first vessel to increase the pressure to its original higher value.

(ii) If solutions of two different concentrations be brought in contact, the solute begins to diffuse from the higher to the lower concentration till the concentration throughout becomes the same. This spontaneous action is also unidirectional and would continue till the *equilibrium* is reached. Further, by itself the solute would not migrate back to make one portion more concentrated than the rest.

(iii) If a hotter body A at temperature T_1 comes in contact with a colder body B at temperature T_2 , ($T_1 > T_2$), we always find heat flowing from A to B until the temperatures of both A and B become equal, i.e., a *thermal equilibrium* is attained. Here also, heat does not flow from B to A , i.e., the transfer is unidirectional and irreversible.

(iv) It is a common experience that a liquid will always flow freely from a higher to a lower level until the levels are equalised, i.e., *mechanical equilibrium* is reached. This is also an irreversible process.

(v) Metallic copper is deposited with evolution of heat when copper sulphate solution is brought in contact with zinc, and the reaction continues until the *chemical equilibrium* is attained. The broad fact is that a chemical reaction would always proceed in a direction to reach the equilibrium.

Many other examples may be given. But all these spontaneous processes take place in one direction and are irreversible. Every system naturally moves towards the equilibrium state. The Second Law which is formulated to record our experience about the direction of changes, may therefore be stated as.

"All spontaneous processes are irreversible" or, we may also say,

"All spontaneous processes tend to equilibrium."

If we confine our attention to a specific case, namely the flow of heat as in our illustration (iii), we can express our experience by the statement given by Clausius, "Heat, of itself, will not pass from a lower to a higher temperature". Or more elegantly stated ;

"It is impossible for a self-acting machine, unaided by any external agency, to convey heat from a body at a low, to one at a high temperature."

Another aspect of the spontaneous processes must also be considered. In all these spontaneous changes, outside effort would be required to effect the reverse change. To take the water to a higher level, to separate the solute from the solution, to produce back the zinc from the solution of zinc sulphate and copper etc., work must be done on the system.

On the other hand, during the spontaneous occurrence of natural processes, seldom any energy is obtained in useful form or work. But nevertheless, by the

introduction of suitable mechanisms, it is possible to obtain useful work when spontaneous processes move towards equilibrium. The mechanism employed to obtain the work may differ from process to process. Thus, the flow of water downwards would yield work if a turbine is installed ; the flow of heat from higher to lower temperature produces work if a heat engine be employed ; the reaction between copper sulphate and zinc would give useful work through a galvanic cell ; the movement of gas from a higher to a lower pressure can be made to do work through a wind-mill etc.

IV.23. The Second Law of Thermodynamics. We have indicated in the previous section the basis of the second law for the guidance of a process in a definite direction. It is also a human experience that when every form of energy, including mechanical work, has a natural tendency to be transformed into thermal energy, the latter shows no natural inclination to be transformed into any other form. Only through the introduction of some mechanism, or machine can we convert heat into other forms. Even then this conversion occurs to a limited extent and not completely. Since heat is readily available, a good deal of human ingenuity is employed to find out the conditions and circumstances under which it would be possible to change heat into work. The guidance as to the conditions under which heat changes into the direction of work would obviously come under the Second Law. For this reason, in enunciating the Second Law we often find the statements refer to the conversion of heat into work. It is now known that two conditions must be fulfilled to utilise heat for useful work.

1. A contrivance or mechanism, commonly called the thermodynamic engine, is essential. Without the aid of an engine the conversion of heat into work is impossible. Further, the engine must work in a reversible cyclic process.

2. The engine must operate between two temperatures. It will take up heat at a higher temperature, convert a portion of it into work and give up the rest of the heat to a body at lower temperature.

Now suppose we have, for an engine, a cylinder with a piston containing x gm-moles of an ideal gas at temperature T same as that of the surroundings. Let the gas expand isothermally from a volume V_1 to a volume V_2 . There would be no change in internal energy, for the gas is ideal. The heat absorbed from

the surroundings will be completely converted into work dW , $\left(= xRT \ln \frac{V_2}{V_1} \right)$,

in accordance with the first law. Here is then a case where dQ quantity of heat from the surroundings is completely converted into work dW . But when this has been achieved, the external agency, (the engine), has suffered a change in volume from V_1 to V_2 . It is thus an experience that complete conversion of heat into work is impossible without leaving a permanent change elsewhere.

If we want to repeat the performance, the gas must be made to come back to its original volume and pick up heat again from the surroundings during expansion. To bring the gas to its original volume V_1 from V_2 , we must perform isothermal work of compression equal to $-xRT \ln \frac{V_2}{V_1}$, the same that we obtained before.

The net result is that the engine, working in a cycle at a temperature same as that of the source of supplier of heat (in this case of the surroundings), would produce no work. It is now a fundamental fact of experience that under isothermal conditions no engine can convert heat into work. That is why we cannot run our tram cars or motor cars with the heat of the surrounding air, or we cannot utilise the vast amounts of ocean-heat to move our ships. This experience has been stated as :

(i) *It is impossible by an inanimate material agency (an engine) to derive mechanical effect (work) from any portion of matter by cooling it below the temperature of the coldest of the surroundings (Kelvin).*

(ii) *It is impossible to construct an engine, working in a cycle, which would produce no effect except the raising of a weight and the cooling of a heat reservoir (Planck).*

A little thought would reveal that all these statements essentially convey the same meaning.

We have so far seen, heat obtained from a supplier at the same or lower temperature than that of the engine cannot be transformed into work in a cyclic process. But when heat flows from a reservoir at higher temperature (called the source) to a reservoir at lower temperature (called the sink), it can be transformed into work with the intervention of an engine. The engine would pick up Q calories from the source, transform only a portion of it into work W and return the rest of the heat Q' to the sink. According to the first law then

$$W = Q - Q'$$

The amount of work to be obtained from a given amount of heat will depend on the nature of the engine and the temperatures of the source and the sink. We can define the efficiency of an engine, in the usual way :

$$\eta = \frac{\text{work produced}}{\text{heat supplied}} = \frac{W}{Q} = \frac{Q - Q'}{Q} \quad \dots \text{(IV.38)}$$

$$\eta = 1 - \frac{Q'}{Q} \quad \dots \text{(IV.39)}$$

Its utility, in practice, can be realised by considering a cyclic process. The most ideal of such cyclic processes would be the Carnot's cycle.

IV.24. Carnot's Cycle. It was the brilliant French engineer Sadi Carnot (1824) who explained clearly how and to what extent work is obtainable from heat. Carnot started with two essential pre-requisites. Firstly, to estimate the work obtained from heat during its passage from a higher to a lower temperature, the external agency (the engine) must come back to its original state so as to exclude any work involved in its own change. That is, the engine must operate in complete cycles. Secondly, to obtain maximum work in a cycle of operations, every step should be carried out in a reversible fashion.

The typical Carnot's cycle consists of four successive operations using one gm-mole of a perfect gas as the working substance. We take the gas enclosed in a cylinder fitted with a frictionless piston. To start with, the cylinder containing the gas is kept in a large thermostat at the higher temperature (source) and suppose the volume of the gas be V_1 .

Operation 1. The gas is allowed to expand isothermally and reversibly from the volume V_1 to the volume V_2 .

The heat absorbed by the gas = Q (say),

The work done by the gas = $RT \ln \frac{V_2}{V_1}$,

Since the gas is ideal, we know, $Q = RT \ln \frac{V_2}{V_1} \quad \dots \text{(IV.40)}$

Operation 2. The cylinder is next taken out of the thermostat and kept in a thermally insulated enclosure. The gas is allowed to expand further from volume V_2 to volume V_3 adiabatically and reversibly until the temperature falls down to that of the sink T' .

The heat absorbed by the gas = nil.

The work done by the gas = $C_V(T - T')$

(C_V is the heat capacity of the gas.) $\dots$ (from IV.33)

Operation 3. The cylinder is then placed in a thermostat at temperature T' (sink); the gas is compressed isothermally and reversibly until the volume changes to V_4 from V_3 .

The heat given out by the gas = Q' (say)

The work done by the gas = $RT' \ln \frac{V_4}{V_3}$

[Since V_4 is smaller than V_3 , the work is negative which means work is done on the gas]

Operation 4. The cylinder is now thermally isolated as in operation 2. The gas is then adiabatically and reversibly compressed to its initial volume V_1 and its original temperature T is attained. The gas thus comes back to its initial state.

The heat absorbed by the gas = nil

The work done by the gas = $-C_V(T-T')$

These operations may be represented by a P - V diagram as in Fig. IV.12. The total area enclosed within $ABCD$ would represent the work obtained in the cyclic process.

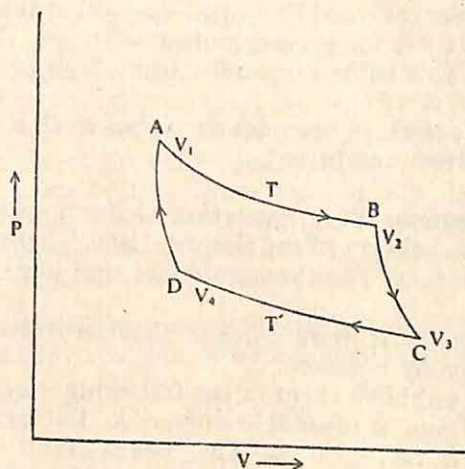


FIG. IV.12. Carnot's cycle

The net work done by the gas in the complete cycle,

$$\begin{aligned} W &= RT \ln \frac{V_2}{V_1} + C_V(T-T') + RT' \ln \frac{V_4}{V_3} - C_V(T-T') \\ &= RT \ln \frac{V_2}{V_1} - RT' \ln \frac{V_3}{V_4} \end{aligned}$$

But considering the adiabatic changes in operations 2 and 4, we have from Sec IV.14.,

$$(a) \quad TV_2^{\gamma-1} = T'V_3^{\gamma-1}$$

and

$$(b) \quad TV_1^{\gamma-1} = T'V_4^{\gamma-1}$$

dividing,

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\begin{aligned} \text{Therefore the net work, } W &= RT \ln \frac{V_2}{V_1} - RT' \ln \frac{V_3}{V_1} \\ &= R(T-T') \ln \frac{V_2}{V_1} \end{aligned} \quad \dots (IV.41)$$

The efficiency of the process is given by equation (IV.38),

$$\eta = \frac{W}{Q} = \frac{R(T-T') \ln \frac{V_2}{V_1}}{RT \ln \frac{V_2}{V_1}} = \frac{T-T'}{T} = 1 - \frac{T'}{T} \quad \dots (IV.42)$$

$$\text{and} \quad W = Q \frac{T-T'}{T} = Q \frac{\Delta T}{T} \quad \dots (IV.43)$$

This relation expresses the maximum amount of work obtainable from the heat flowing from T to T' . This is the mathematical form of the Second Law

Notes : (i) Between two given temperatures, only $\frac{\Delta T}{T}$ fraction of the total heat supplied is obtainable as work.

(ii) $W = Q$, only when $T' = 0$. That is, if the engine works between absolute zero and a higher temperature, complete conversion of heat into work would be possible. Since this cannot be realised in practice, the complete transformation of heat into work is impracticable ; the efficiency is thus always less than unity.

(iii) The efficiency of the engine depends only on the temperatures of the source and the sink (eq. IV.42). For a given source, the lower the temperature of the sink the greater will be the yield of work. Very often the sink is at the room temperature. In such a case, for greater output of work, the temperature of the source should be high. This is the reason for using high pressure steam in boilers for production of power.

(iv) When $T = T'$, work W becomes zero. No work is available by operating an engine under isothermal conditions.

IV.25. The Carnot Theorem. Two important deductions are easily arrived at on the assumption of the validity of the Second Law. These deductions are embodied in the Carnot's theorem. The theorem states that working between the same temperature limits,

(i) *a reversible engine is more efficient than an irreversible one* and (ii) *all reversible engines are equally efficient*.

We can proceed to establish them in the following way. (i) Suppose we have an irreversible engine I and a reversible engine R . Let us assume the efficiency of I greater than that of R , i.e., $\eta_I > \eta_R$. This means that if a source supplies same quantity of heat to both the engines, greater amount of work will be obtained from I than from R . Suppose the engines operate between the source at temperature T and the sink at temperature T' . Now the energy changes with the two engines would be as follows :

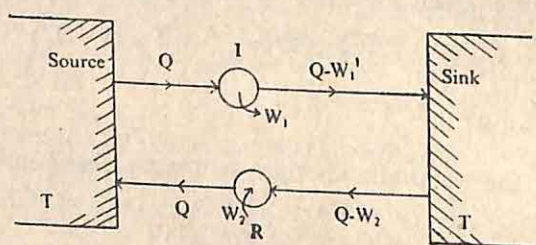


FIG. IV.13

Engine I

Heat supplied by source	$= Q$
Work performed	$= W_1$
Heat rejected to sink	$= Q - W_1$

Engine R

Heat supplied by source	$= Q$
Work performed	$= W_2$
Heat rejected to sink	$= Q - W_2$

We know, $W_1 > W_2$ and hence, $Q - W_1 < Q - W_2$.

Let us now carry out a cyclic process in which engine I would perform the forward process. It will be supplied with heat Q from the source and it will yield W_1 work and reject the rest of the heat to the sink ; and the reverse process will be done by the engine R which taking up heat $Q - W_2$ from the sink and having W_2 units of work done on it, would return heat Q to the source. In this complete cyclic process, the source has not ultimately lost any heat. But the coupled engines have yielded work $W_1 - W_2$ and the net heat lost by the sink is $(Q - W_2) - (Q - W_1)$, which is equivalent to the work obtained. That means we have been able to convert completely the heat taken from the sink at the lower temperature (Fig. IV.13).

This is contrary to the Second Law and is improbable. Therefore, the efficiency of the reversible engine cannot be less than the efficiency of the irreversible one.

(ii) The second part of the theorem can also be proved in a similar way. Suppose two reversible engines R_1 and R_2 work between the source (T) and the sink (T'). Let us assume, one of the engines, say R_1 , is more efficient than R_2 . As before, let us couple the two engines to carry out a cyclic process. The engine R_1 takes up heat Q from the source, yields work W_1 and rejects $(Q - W_1)$ heat to the sink, while the engine R_2 performs the opposite process, taking $(Q - W_2)$ units of heat from the sink with W_2 units of work done on it, and returning heat Q back to the source. Since $\eta_{R_1} > \eta_{R_2}$, therefore $W_1 > W_2$. The source has not, at the completion of the cyclic process, lost any heat. The net result is that $W_1 - W_2$ units of work have been produced. There is a loss of $(Q - W_2) - (Q - W_1) = W_1 - W_2$ units of heat from the sink. The heat of the lower temperature sink is thus completely converted into work, which is against the Second Law. Thus engine R_1 cannot be more efficient than R_2 . Similarly, R_2 cannot have greater efficiency than R_1 . That is both the engines are equally efficient. Hence all reversible engines working between the same temperatures must be equally efficient. Since we have not taken into consideration the nature of the working substance of the engine, we may also say that the efficiency of the Carnot engine is independent of the nature of the working substance.

Problems : (1) A Carnot engine working between 0°C and 100°C takes up 840 joules from the high temperature reservoir. Calculate the work done, the heat rejected and the efficiency.

$$(a) \text{ Work done } W = Q_1 \times \frac{\Delta T}{T} = 840 \times 10^7 \times \frac{100}{373} = 2.25 \times 10^9 \text{ ergs.}$$

$$(b) \text{ Heat rejected } Q_2 = Q_1 \cdot \frac{T_2}{T_1} = \frac{840}{4.2} \cdot \frac{273}{373} = 146 \text{ calories.}$$

$$(c) \text{ Efficiency, } \eta = \frac{T_1 - T_2}{T_1} = \frac{100}{373} = 0.268.$$

(2) An engine works in a Carnot's cycle between 27°C and 127°C , the work output per cycle is 300 Kgm-metres. Calculate the heat supplied to the engine from the source.

Let heat supplied = Q calories.

$$\text{Since } W = Q \frac{\Delta T}{T},$$

$$\text{expressed in ergs, } 300 \times 1000 \times 100 \times 981 = Q \times 4.2 \times 10^7 \times 100/400$$

$$\text{or } Q = 7803 \text{ calories.}$$

ENTROPY

In order to make a more thorough understanding of the Second Law, it is necessary to introduce another thermodynamic function, *entropy*. We shall first attempt to follow the steps which lead us to the concept of this function.

IV.26. dq is not a Perfect Differential but dq/T is a Perfect Differential. We have seen in Sec. IV-7, that the amount of heat dq absorbed or evolved during the change of a system from one given state to another given state depends on the way the change of the system is carried out, i.e., dq depends on the path of the transformation. Therefore dq cannot be a perfect differential. To illustrate :

(i) Suppose a quantity of a perfect gas (say 1 mole) undergoes a *reversible* expansion from volume V_1 to V_2 when the temperature changes from T_1 to T_2 . From the first law,

$$dq = dU + PdV$$

$$\text{or } \int_I^{II} dq = \int_I^{II} dU + \int_I^{II} PdV = \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2} RT d \ln V \quad \dots \text{ (IV.44)}$$

$$\text{or} \quad \int_I^{II} dq = C_V(T_2 - T_1) + \int_{V_1}^{V_2} RT d \ln V$$

The integral on the right-hand side, $\int_{V_1}^{V_2} RT d \ln V$ cannot be evaluated unless we know the relation between T and V . If T be constant (*i.e.*, isothermal change), the integral will have one value, and if T changes during the process, the integral will have different values. Thus the magnitude of $\int_I^{II} dq$ depends on the way the expansion is carried out.

Now, dividing the equation (IV.44) by T , we have

$$\int_I^{II} \frac{dq}{T} = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_2} R d \ln V = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

That is the $\int \frac{dq}{T}$ for a given change from state I to state II can be evaluated without any reference to the path of the transformation. Hence $\int \frac{dq}{T}$ is independent of the way the change is carried out though $\int dq$ is not. It is to be remembered that the heat-change dq takes place in a reversible way.

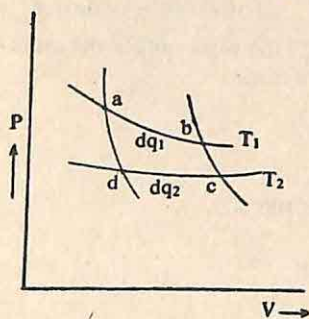


FIG. IV.14. The Carnot's Cycle

(ii) We can also arrive at this conclusion in other ways. Consider a Carnot cycle as represented in Fig. IV.14. in which ab and cd are the isothermals at temperatures T_1 and T_2 ; bc and da are the adiabatic stages. Let dq_1 be the heat supplied to the working system at T_1 and dq_2 be the heat rejected by it to the sink at T_2 . All steps are *reversible*. We know, in a Carnot cycle,

$$\frac{dq_1 - dq_2}{dq_1} = \frac{T_1 - T_2}{T_1} \quad \text{or} \quad \frac{dq_1}{T_1} = \frac{dq_2}{T_2} \quad \dots \text{(IV.45)}$$

(dq_2 is negative as it is rejected by the system).

Now let us confine our attention only to the change of the system from the point a to the point c and attempt to find out the ratio of the heat-change to the temperature at which the thermal change occurs. We can proceed from a to c either along abc or along adc .

Along the path abc , we have the isothermal ab , when heat-change dq_1 takes place at T_1 , followed by adiabatic change bc having no heat-change. Hence,

$$\frac{\text{heat-change}}{\text{temp.}} = \frac{dq_1}{T_1} + 0 = \frac{dq_1}{T_1}$$

Along the path adc , we have the adiabatic ad having no thermal change, but along the isothermal dc , remembering reversibility, heat absorbed would be dq_2 at temperature T_2 . Hence,

$$\frac{\text{heat-change}}{\text{temp.}} = 0 + \frac{dq_2}{T_2} = \frac{dq_2}{T_2}$$

But we know,

$$\frac{dq_1}{T_1} = \frac{dq_2}{T_2}$$

That is, the ratio of the heat change to the temperature, $\frac{dq}{T}$, is the same whatever may be the path followed by the system in its *reversible* change. Hence $\frac{dq}{T}$ is a perfect differential.

IV.27. Definition of Entropy. The heat-change dq and the temperature T are thermodynamic quantities. Therefore, we can say that the system has a thermodynamic function whose change, measured by $\frac{dq}{T}$, is independent of the path of the transformation of the system. This function has been called *entropy* by Clausius and is denoted by the symbol S . Its change dS is measured by the ratio of the heat-change and the temperature at which the heat-change occurs, i.e.,

$$dS = \frac{dq_{rev}}{T} \quad \dots (IV.46)$$

If the heat-change takes place at different temperatures, then

$$dS = \frac{dq_1}{T_1} + \frac{dq_2}{T_2} + \frac{dq_3}{T_3} + \dots = \Sigma \frac{dq_{rev}}{T}$$

or

$$\int dS = \int \frac{dq_{rev}}{T}$$

We can now say :

- (i) Entropy S is a thermodynamic function whose magnitude depends only on the parameters of the system and can be expressed in terms of (P, V, T) .
- (ii) The entropy-change dS is a perfect differential. Its value depends only on the initial and final states of the system, independent of the path of the change. The entropy-change is measured by the reversible heat-change of the system divided by the temperature in absolute scale, i.e., $dS = dq/T$.
- (iii) Absorption of heat increases the entropy of the system. The rejection of heat by the system leads to a decrease in its entropy. During adiabatic changes, ($dq = 0$), the entropy-change is zero. The adiabatic changes are called *iso-entropic* changes.

IV.28. Entropy-change in a Carnot Cycle. Let us return to the Carnot cycle (Fig. IV.14). We have seen, in equation IV.45, that

$$\frac{dq_1}{T_1} = \frac{dq_2}{T_2} ; \text{ or } \frac{dq_1}{T_1} + \frac{-dq_2}{T_2} = 0$$

where dq_1 is the heat received from the source and dq_2 is the heat given up to the sink. Hence $-dq_2$ means heat absorbed. We can then rewrite the above relation as

$$\frac{dq_1}{T_1} + \frac{dq_2}{T_2} = 0 \quad \dots (IV.47)$$

where dq -terms stand for heat-changes containing their own signs.

Along the adiabatic steps bc and da heat-changes do not occur. So the sum total of entropy-changes for the entire Carnot's cyclic process is

$$\oint dS = \frac{dq_1}{T_1} + \frac{dq_2}{T_2} = 0$$

The integral sign $\oint$ denotes the summation over the complete cycle. Hence, the net increase in entropy in a Carnot's cycle is zero: All the steps are reversible,

IV.29. Change of Entropy in any Reversible Cycle. Consider a system undergoing a reversible change along the path ab in the P - V indicator diagram (Fig. IV.16).

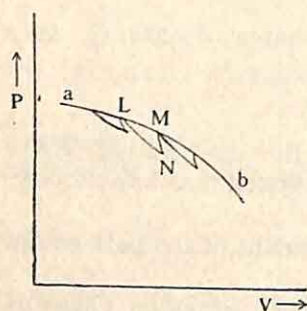


FIG. IV. 16

Let us confine our attention to an infinitesimal change LM in the path ab . This small change may be supposed to be composed of an isothermal change LN followed by an adiabatic change NM . In this way, the entire change ab may be regarded as composed of alternate isothermal and adiabatic changes.

Now suppose we have a reversible cyclic process, not necessarily a Carnot's cycle, represented by $abcd$ in Fig. IV.17. We may regard the changes abc as well as cda consisting of large number of infinitesimal isotherms followed by adiabatics. The adiabatics along abc may be joined to those along cda . This would turn the complete cyclic process into a large number of Carnot's cycles. Take any one of the Carnot's cycles, say $pqrs$, where pq and rs are the isotherms with heat-changes, dq_1 at T_1 and dq_2 at T_2 respectively. The heat-changes along the adiabatics qr and ps are nil.

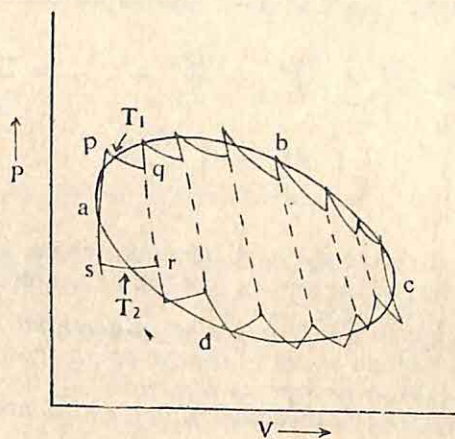


FIG. IV.17

Then, for the Carnot's cycle $pqrs$, we have,

$$\frac{dq_1}{T_1} + \frac{dq_2}{T_2} = 0$$

for other Carnot's cycles, similarly,

$$\frac{dq'_1}{T_1} + \frac{dq'_2}{T_2} = 0; \quad \frac{dq''_1}{T_1} + \frac{dq''_2}{T_2} = 0; \quad \text{and so on.}$$

Hence for the complete reversible cyclic process,

$$\Sigma \frac{dq}{T} = 0; \quad \text{or} \quad \oint \frac{dq}{T} = 0.$$

$$\oint dS = 0.$$

... (IV.48)

i.e., In any reversible cyclic process, the net increase in entropy of the system is zero.

IV.30. Entropy-change of the Universe. When we speak of the entropy change of a cyclic process, we consider only the working system but do not take into account the entropy-changes in the source and the sink or the surroundings. When heat-transfer takes place, the surroundings also gain or lose heat and so their entropies also change. The total entropy-change which would cover the entropy-

changes in the working system as also in the surroundings is named the *entropy-change of the universe*. Hence the entropy-change of the universe,

$$\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Let us consider the Carnot's reversible cycle (Fig. IV.12), in which the surroundings are the source and the sink. Now,

$$\text{the loss of entropy of the source} = \frac{dq_1}{T_1}$$

$$\text{the gain of entropy of the sink} = \frac{dq_2}{T_2}$$

Net entropy-change of the surroundings,

$$\Delta S_{\text{surroundings}} = \frac{dq_1}{T_1} + \frac{dq_2}{T_2} = 0 \quad (\text{eqn. IV.47})$$

(dq -terms include their own signs).

We already know, $\Delta S_{\text{system}} = 0$

$$\therefore \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0.$$

The net entropy change in a reversible cyclic process is zero.

Again, the net entropy-change of the universe for a single reversible process is also zero. When the source supplies heat dq_1 to the engine, reversibly,

$$\text{the increase of entropy of the engine} = \frac{dq_1}{T_1}$$

$$\text{the loss of entropy of the source} = \frac{dq_1}{T_1}$$

That is, the net entropy change is *nil*.

The same result is obtained when the engine rejects heat to the sink.

IV.31. Entropy-change and Irreversible Processes. The entropy-change of a system in passing from a given state I to a given state II is always the same and is independent of the way in which the system changes, since entropy is a function of the state only. It is immaterial whether the path of transformation is reversible or irreversible; the entropy-change will be the same between two given states. Only if the path is reversible, we know the entropy-change would be given by

$$\Delta S = S_{II} - S_I = \int_I^{II} \frac{dq_{rev}}{T}$$

Hence in order to compute the entropy-change of a system in an irreversible process, we may conceive of taking the system from state I to state II along *any reversible path* and then divide the heat absorbed by the system at each point by the temperature of the system and summing up the quotients. Any reversible path will do since ΔS will be same for all reversible paths.

Let us now consider some irreversible processes.

(a) *An irreversible cyclic process.*

Consider a cyclic process, similar to that of Carnot cycle, in which one or more of its stages are performed irreversibly. Let ABCD denote the cycle in Fig. IV.18, in which AB and CD are the isothermal stages. Let us further suppose, the absorption of heat dq_1^* by the system at temp. T_1 from the source along AB is irreversible. The rest of the stages are carried out

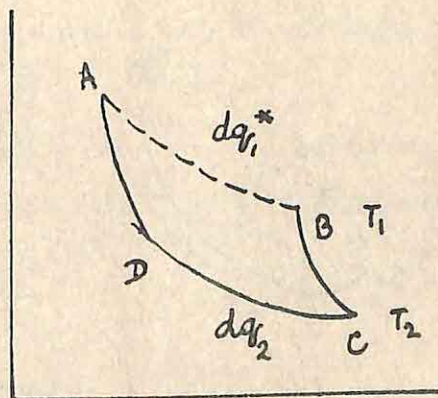


FIG. IV.18

reversibly. The asterisk (*) would indicate the irreversibility, otherwise the transformation is reversible. The heat dq_2 is given up to the sink at temp. T_2 along CD .

This is an irreversible cycle and hence the efficiency of the engine is less than that of the Carnot cycle, or,

$$\frac{dq_1^* - dq_2}{dq_1^*} < \frac{T_1 - T_2}{T_1} \quad \text{or} \quad \frac{dq_2}{T_2} - \frac{dq_1^*}{T_1} > 0 \quad \dots (i)$$

When the cycle is completed, the engine has returned to its initial state,

$$\therefore \Delta S_{\text{system}} = 0$$

Now consider the surroundings and find out the q/T terms.

It is $\frac{-dq_1^*}{T_1}$ for the source and $\frac{dq_2}{T_2}$ for the sink.

Hence, for the surroundings, $\sum \frac{Q}{T} = \frac{dq_2}{T_2} - \frac{dq_1^*}{T_1}$, which is, from (i), greater than zero, i.e., positive.

The heat-change of the sink is reversible. The heat dq_1^* from the source was taken by the system irreversibly. The source has lost dq_1^* and its entropy has decreased. The entropy-change of the source from $A \rightarrow B$ would be evaluated as stated earlier by supposing the loss of heat dq_1 occurred reversibly and consequently $\Delta S_{\text{source}} = -dq_1^*/T_1$.

$$\text{Or, we can say, } \Delta S_{\text{surr.}} = \frac{dq_2}{T_2} - \frac{dq_1^*}{T_1} > 0$$

In this irreversible cyclic process, therefore

$$\Delta S_{\text{univ.}} = \Delta S_{\text{system}} + \Delta S_{\text{surr.}} = 0 + \Delta S_{\text{surr.}} > 0.$$

In an irreversible cyclic process, there would occur a net increase in entropy.

Next consider a general cyclic process involving an irreversible step. We know in a reversible cyclic process,

$$\frac{dq_1}{T_1} + \frac{dq_2}{T_2} = 0, \quad (dq\text{-terms involve their own signs})$$

$$\text{i.e.,} \quad \oint \frac{dq}{T} = 0 \quad (\text{reversible})$$

In an irreversible cycle,

$$\frac{dq_1 + dq_2}{dq_1} < \frac{T_1 - T_2}{T_1}$$

hence

$$\frac{dq_1}{T_1} + \frac{dq_2}{T_2} < 0$$

This is often referred to as Clausius inequality.

Let $acbdba$ be the cyclic process in which the change acb is irreversible. But the transformation bda is completed by a reversible path. [Fig. IV.19].

We can then say.

$$\int_a^b \frac{dq^*}{T} + \int_b^a \frac{dq}{T} < 0$$

Since heat dq^* is absorbed irreversibly, the magnitude of $\int_a^b \frac{dq^*}{T}$ will depend on the path

and hence indefinite. But $\int_b^a \frac{dq}{T}$ which relates

to a reversible change bda and is definite and is equal to entropy-change, $S_a - S_b$.

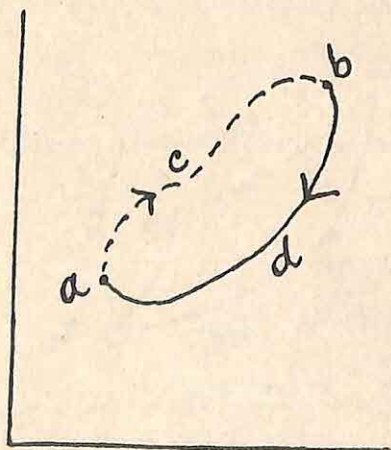


FIG. IV.19

$$\therefore \int_a^b \frac{dq^*}{T} + S_a - S_b < 0$$

$$\text{or} \quad S_b - S_a - \int_a^b \frac{dq^*}{T} > 0$$

Now $S_b - S_a$ is the entropy-change of the system in the irreversible change acb , and it is greater than $\int_a^b \frac{dq^*}{T}$.

The question now arises that what would be the entropy-change of the surroundings in the irreversible path acb . For this, let us restore the surroundings to its original state from b to a by adding dq^* heat *reversibly* at appropriate temperature. The entropy-change in the surroundings along bca then would be

$$\sum \frac{dq^*}{T} = \int_b^a \frac{dq^*}{T} = - \int_a^b \frac{dq^*}{T}$$

The rest of the cyclic process is reversible and hence the entropy-changes for surroundings and system there are equal and opposite.

Thus for the irreversible process acb ,

$$\Delta S_{\text{system}} = S_b - S_a$$

$$\Delta S_{\text{surr}} = - \int_a^b \frac{dq^*}{T}$$

$$\therefore \Delta S_{\text{universe}} = S_b - S_a - \int_a^b \frac{dq^*}{T} = +\text{ve quantity.}$$

Hence, in any irreversible process, or in an irreversible cycle there would be a net increase in the entropy of the system and surroundings.

We can say, for an irreversible process,

$$\Delta S_{\text{univ.}} = \Delta S_{\text{system}} + \Delta S_{\text{surr.}} > 0$$

It is easy to see that during an irreversible process the entropy of an isolated system will also always increase.

For an irreversible process we have seen,

$$\Delta S_{\text{system}} + \Delta S_{\text{surr.}} > 0.$$

Since the system is isolated *i.e.*, thermally insulated from the surroundings, the latter will have no change in entropy *i.e.*, $\Delta S_{\text{surr.}} = 0$. Hence

$$\Delta S_{\text{system}} > 0.$$

That is, in an irreversible adiabatic transformation, the system will increase in its entropy.

(b) *Irreversible flow of heat.* Let a heat reservoir at temperature T_1 be brought in contact with a second reservoir at a lower temperature, say at T_2 . A small quantity of heat, say q , passes irreversibly from A to B .

The decrease in entropy of $A = q/T_1$

The increase in entropy of $B = q/T_2$

$$\therefore \text{net entropy-change} = \frac{q}{T_2} - \frac{q}{T_1} = q \frac{T_1 - T_2}{T_1 T_2} = +\text{ve quantity.}$$

The irreversible flow of heat leads to an increase in entropy.

We can also devise a reversible method for transferring q heat from A to B in a reversible way and then evaluate therefrom the entropy-change. Take an ideal gas in a cylinder and keep it with the hot reservoir at T_1 and reversibly q heat is taken up. [For simplicity we presume that the heat reservoirs have large heat capacities so that heat-change q scarcely affects their temperatures.] The gas is then removed from A and allowed to expand reversibly and adiabatically until its temperature is T_2 . It is then brought in contact with reservoir B and compressed isothermally till q heat is given to B .

The net entropy-change of the two reservoirs $= \frac{q_2}{T_2} - \frac{q_1}{T_1}$ which is the same as before and positive.

The net entropy change of the gas-system $= \frac{q_1}{T_1} - \frac{q_2}{T_2}$, hence $-ve$.

The total entropy-change of the gas and reservoirs together is nil, for the whole is a completely reversible cyclic process.

(c) *Irreversible free expansion of an ideal gas.* Suppose n gm moles of an ideal gas expands at temp T freely from volume v_1 to volume v_2 . It is free expansion,

no work is involved, no heat flows into the gas in this process. So, $\frac{dq}{T}$ cannot be

directly obtained. The entropy-change in the process has to be computed by devising a reversible process between the two given states. Since in the actual process temperature remained unaltered, let us consider the reversible isothermal expansion of the gas from volume v_1 to volume v_2 and find out the entropy-change therefrom. From the 1st Law,

$$dq_{\text{rev.}} = du + dw = 0 + nRT \ln \frac{v_2}{v_1}$$

$$\therefore ds = \frac{dq_{\text{rev.}}}{T} = nR \ln \frac{v_2}{v_1}$$

since $v_2 > v_1$, ds is positive; the entropy of the gas in its free expansion would increase.

Entropy and the Second Law. We are thus led to believe that in every irreversible process if we sum up all the entropy-changes in the different parts of the system and the surroundings, there would be a net rise in the total entropy. In nature, the processes occurring spontaneously are all irreversible. Therefore, broadly speaking the spontaneous changes in nature would always cause entropy-increase. Thus, the fall of an apple from a tree, the flowing of a river downhill, the rusting of iron, the mixing of two gases and so on, are all spontaneous and irreversible changes and these would add to an increase in entropy. In other words, we may say, a natural process will take place in a direction in which the entropy would increase; or, a process which would not raise the entropy of the universe, will not spontaneously occur. However, in all such changes the energy may be transformed but the total quantity remains constant. This is why the two laws of thermodynamics are often stated as,

(a) First Law : The net energy of the universe remains constant.

(b) Second Law : The net entropy of the universe tends to a maximum.

IV.32. Entropy and the Available work. A little reflection would reveal that with the progress of an irreversible process, the possibility of obtaining work from a system diminishes.

Suppose there are three heat reservoirs at high temperatures T_1 , T_2 and T_3 such that $T_1 > T_2 > T_3$. There is also another heat reservoir, the sink, at a lower temperature T (say, room temperature). Let there be a reversible engine working

between the 1st reservoir at T_1 and the sink at T and let the quantity of heat supplied to the engine from the source at T_1 be Q . Then we know that the maximum work available would be,

$$W_1 = Q \left[1 - \frac{T}{T_1} \right]$$

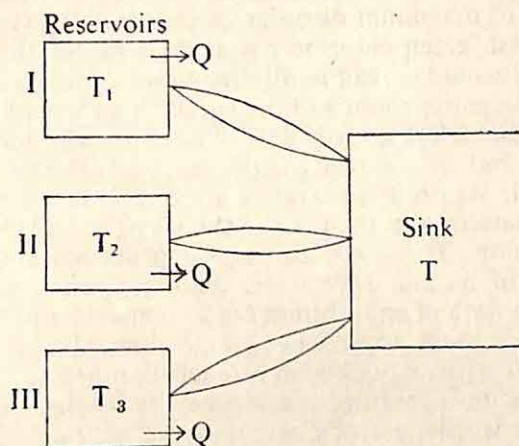


FIG. IV.20

Let us imagine next that the heat Q have flown down irreversibly from the 1st reservoir at T_1 to the second reservoir at T_2 by conduction or radiation before being received by the engine. Now, suppose we engage a reversible engine to work between the second reservoir and the sink and let the engine receive the same heat Q from this source. The maximum work available would be,

$$W_2 = Q \left[1 - \frac{T}{T_2} \right]$$

Similarly, if the heat Q flows down irreversibly to the third reservoir at T_3 and then supplied to a reversible engine as before, the maximum available work would be

$$W_3 = Q \left[1 - \frac{T}{T_3} \right]$$

The amount of work available from the same quantity of heat supplied are different. Since $T_1 > T_2 > T_3$, we have $W_1 > W_2 > W_3$.

This means that the lower the temperature of the reservoir to which the amount of heat Q would irreversibly flow, the lesser would be the yield of work. If in this way the same heat Q flows down to a reservoir at T (the same as that of the sink), the available work, $\left[W = Q \left(1 - \frac{T}{T} \right) \right]$, would be nil. Though the

quantity of heat Q remains the same, yet due to its irreversible transfer from the higher to the lower temperature, its potentiality of being converted into work is diminished or degraded. This is why the first law is often called as the law of conservation of energy and the second law as the law of degradation of energy.

Let us come back to the question of the availability of work. Due to irreversible flow of heat from T_1 to T_2 the decrease in the amount of available work,

$$\Delta W = W_1 - W_2 = Q \left[\frac{T}{T_2} - \frac{T}{T_1} \right] = QT \frac{T_1 - T_2}{T_1 T_2} \quad (\text{a + ve quantity})$$

Again, due to the irreversible flow of heat, the increase of entropy,

$$\Delta S = \frac{Q}{T_2} - \frac{Q}{T_1} = Q \cdot \frac{T_1 - T_2}{T_1 T_2}$$

By substitution, $\Delta W = T \Delta S$.

That is, the energy rendered unavailable as work is proportional to the entropy-increase. The higher the level of entropy, the lesser would be the availability of work. The entropy-rise is a measure of the unavailable work.

IV.33. The Physical Concept of Entropy. That a system left to itself will gradually pass into a state of equilibrium is our common experience. The state of equilibrium really means a state of maximum disorder or chaos. For example, if we let loose a quantity of yellowish green chlorine gas at a corner of the floor of the room, the gas though heavy would spread in all directions until it would be most chaotically distributed in the entire room and the equilibrium would be reached. Exactly similar are the processes when a syrup gets diluted by diffusion in the water added to it or the red hot end of a poker distributes its heat and raises the temperature of the entire rod. Again if we arrange a number of red and black balls on a tray in a particular pattern and then shake the tray the balls would mix up in the most disordered fashion. These are all natural processes and never we find the opposite to happen in nature. Moreover, these processes which always have a tendency to attain the state of equilibrium are irreversible and thus lead to entropy-increase. The more a system approaches equilibrium, the greater is the disorder and irreversibility and when equilibrium is reached, it has the maximum disorder. The entropy also goes on increasing and reaches its maximum value at the equilibrium state. In other words, entropy is a measure of the disorder of the system or it may be called a measure of the mixed-up-ness of the system.

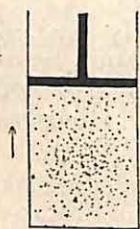


FIG. IV.21.

Conversely, when we attempt to bring order to a system entropy diminishes. Suppose we have a gas in equilibrium confined in a cylinder with a piston. The piston is now somewhat raised upwards increasing the volume slightly. All the molecules, in whatever direction those might be moving, are subjected now to a tendency of motion in the direction of the piston. This is indirectly an attempt to bring some order. In consequence the gas is cooled and the entropy decreases. In the crystalline state of pure substances the entropy becomes the least as there is perfect order or least chaos.

When a solid melts, the allowed molecular positions increase and there is an increase in disorder or chaos. Hence, there would be an increase in entropy. The disorder increases further when liquid vaporises for the same reason. Thus, we see,

(a) in the liquefaction of benzene : $\text{C}_6\text{H}_6(s) \rightarrow \text{C}_6\text{H}_6(l)$

$$\Delta S = \frac{L_f}{T} = \frac{78 \times 30.3}{278.3} = 8.4 \text{ e.u.}$$

and (b) in the vaporisation of benzene : $\text{C}_6\text{H}_6(l) \rightarrow \text{C}_6\text{H}_6(g)$

$$\Delta S = \frac{L_f}{T} = \frac{78 \times 94.3}{353.2} = 20.8 \text{ e.u.}$$

In both the cases, there is an increase in entropy.

We have seen, in the previous section, that the amount of the available work from a given heat-source diminishes with the fall in temperature of the source. When the source and the sink are in thermal equilibrium (*i.e.*, same temperature), the entropy increases to the maximum but the available work becomes nil. In other words, the more the source is run down the greater becomes the entropy. Again, if we take a voltaic cell, we can obtain electrical work so long as there is a potential difference between the two electrodes. If the two electrodes are brought to the same potential, the entropy would increase but the cell would be completely run down and would yield no work. This is why the entropy has been considered by Tolman as a measure of the rundown-ness of a system.

IV.34. The Entropy of a Perfect Gas. It is possible to express the entropy of a perfect gas now from the first law. We know, $dq = dU + PdV$.

Dividing both sides by T , we have

$$\frac{dq}{T} = \frac{dU}{T} + \frac{PdV}{T} = C_V \frac{dT}{T} + R \frac{dV}{V} \quad (\text{for 1 gm-mole})$$

$$\text{or} \quad dS = C_V d \ln T + R d \ln V$$

$$\text{or} \quad S = C_V \ln T + R \ln V + S_0 \quad \dots (IV.48)$$

[Where S_0 is a constant ; heat-capacities assumed to remain unaltered.]

Since $C_P - C_V = R$ for a perfect gas, so

$$S = (C_P - R) \ln T + R \ln \frac{RT}{P} + S_0$$

$$\text{or} \quad S = C_P \ln T - R \ln P + S_0' \quad \dots (IV.49)$$

It must be noted here that the value of the constant S_0 or S_0' cannot be obtained from the thermal capacities or the parameters alone. As such, we cannot ascertain the absolute value of the entropy of a perfect gas from classical thermodynamics. But the changes in entropy can be easily determined. Thus, if the temperature of a gas changes from T_1 to T_2 and volume from V_1 to V_2 then, for one gm-mole of the gas,

$$S_1 = C_V \ln T_1 + R \ln V_1 + S_0$$

$$S_2 = C_V \ln T_2 + R \ln V_2 + S_0$$

$$\therefore \quad \Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \dots (IV.50)$$

If the change be an isothermal one, then,

$$\Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}.$$

Real gases : If we take a real gas, say a van der Waals' gas, then in its first approximation ;

$$P = \frac{RT}{V-b}$$

$$\text{So, from the First Law,} \quad \frac{dq}{T} = \frac{dU}{T} + \frac{P}{T} dV$$

$$\text{or} \quad dS = C_V \frac{dT}{T} + \frac{R}{V-b} dV \quad (\text{for 1 gm-mole})$$

Assuming C_V to remain constant,

$$S = C_V \ln T + R \ln (V-b) + S_0'''$$

$$\text{Hence} \quad \Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2-b}{V_1-b}$$

IV.35. Changes in Entropy in some simple processes. The changes in entropy in ordinary processes can be easily calculated as the following examples would show.

(a) Calculate the change in entropy when 10 gms. of tin are heated from 20°C to 300°C . Given, per gram of tin, latent heat of fusion = 14 calories, sp. heats of solid and liquid tin 0.055 and 0.064 respectively ; melting point of tin = 232°C .

(i) Entropy-change in heating 10 gms. of tin from 20°C to 232°C (m.pt),

$$\Delta S_1 = \int_{293}^{505} mc \frac{dT}{T} = 10 \times 0.055 \ln \frac{505}{293} = 0.2994.$$

(ii) entropy-change in the fusion of tin,

$$\Delta S_2 = \frac{\Delta q}{T} = \frac{10 \times 14}{505} = 0.28$$

(iii) entropy-change in heating liquid tin from 232°C to 300°C,

$$\Delta S_3 = \int_{505}^{573} \frac{dq}{T} = \int_{505}^{573} 10 \times 0.064 \frac{dT}{T} = 0.081$$

The total entropy-change, therefore,

$$\Delta S_1 + \Delta S_2 + \Delta S_3 = 0.2994 + 0.28 + 0.081 = 0.6604 \text{ cal per degree C.}$$

(b) Find the increase in the molar entropy of copper when it is heated from 127°C. to 927°C. The molar sp. heat of copper is given by $C_P = 6.2 + 0.0017T$

$$\begin{aligned} \Delta S &= \int_{400}^{1200} \frac{C_P dT}{T} = \int_{400}^{1200} \frac{(6.2 + 0.0017T)}{T} dT \\ &= 6.2 \ln \frac{1200}{400} + 0.0017 (1200 - 400) = 9.77 \text{ calories per degree C.} \end{aligned}$$

(c) Given, specific heat of liquid water = 4180 joules per kg., specific heat of water vapour = $(1670 + 0.49T)$ joules per Kg. and latent heat of vaporisation = 23×10^5 joules per Kg., compute the change in entropy when 100 Kgs. of water at 27°C are converted into superheated steam at 200°C under constant atmospheric pressure.

(i) The entropy-change in heating water from 27°C to 100°C,

$$\Delta S_1 = 100 \int_{300}^{373} C_P d \ln T = 100 \times 4180 \times 2.303 \log \frac{373}{300} = 91082.2 \text{ joules/degree C.}$$

(ii) the entropy-change in vaporisation,

$$\Delta S_2 = 100 \times \frac{23 \times 10^5}{373} = 6.2 \times 10^5 \text{ joules/degree C.}$$

(iii) the entropy-change in heating steam from 100°C to 200°C,

$$\begin{aligned} \Delta S_3 &= 100 \int_{373}^{473} C_P \frac{dT}{T} = 100 \int_{373}^{473} \frac{(1670 + 0.49T)}{T} dT \\ &= 100 \times 1670 \ln \frac{473}{373} + 0.49 \times 100 \times (473 - 373) = 39696 \text{ joules/degree C.} \end{aligned}$$

$$\text{Total entropy-change} = 91082.2 + 6.2 \times 10^5 + 39696 = 7.5 \times 10^5 \text{ joules per degree C.}$$

Mixtures of Gases. When two or more gases are brought in contact, they immediately diffuse into one another and mix up irreversibly. Such a spontaneous irreversible process would lead to an increase in entropy. It is possible to derive for such a mixture an expression of the entropy-change, if the gases be *ideal*.

Let x_A and x_B gm-moles of two gases A and B are mixed at a constant temperature T under a constant pressure P . Before mixing, their entropies are

$$S_A = x_A [C_{pA} \ln T - R \ln P + S_{0A}]$$

$$S_B = x_B [C_{pB} \ln T - R \ln P + S_{0B}]$$

After mixing, the final pressure remaining constant, the partial pressures of A and B may be denoted by P_A and P_B such that $P = P_A + P_B$. The entropies of the two gases in the mixture are

$$S_{Am} = x_A [C_{pA} \ln T - R \ln P_A + S_{0A}]$$

$$S_{Bm} = x_B [C_{pB} \ln T - R \ln P_B + S_{0B}].$$

$$\therefore \text{The entropy-change, } \Delta S_m = S_{A_m} + S_{B_m} - S_A - S_B \\ = -x_A R \ln \frac{P_A}{P} - x_B R \ln \frac{P_B}{P}.$$

The total amount of the mixture is $x_A + x_B$ and the mol-fractions of the components are

$$n_A = \frac{x_A}{x_A + x_B}, \quad n_B = \frac{x_B}{x_A + x_B}$$

$$\therefore n_A = \frac{P_A}{P}, \text{ and } n_B = \frac{P_B}{P}$$

Hence entropy-change per mole of the mixture

$$\Delta S = -\frac{x_A}{x_A + x_B} R \ln \frac{P_A}{P} - \frac{x_B}{x_A + x_B} R \ln \frac{P_B}{P} \\ = -n_A R \ln n_A - n_B R \ln n_B$$

[Since n_A and n_B are less than unity, ΔS is always positive.]

If a number of gases are mixed, then the entropy-change per mole of the mixture may be given by,

$$\Delta S = -R \sum n_i \ln n_i$$

n_i being the mole-fraction of the species i .

Problem : At N.T.P., 2.8 litres of oxygen were mixed with 19.6 litres of Hydrogen: Calculate the increase in entropy.

$$2.8 \text{ litres of oxygen} = \frac{2.8}{22.4} = \frac{1}{8} \text{ gm. mole.}$$

$$19.6 \text{ litres of hydrogen} = \frac{19.6}{22.4} = \frac{7}{8} \text{ gm. mole ; Total} = 1 \text{ gm. mole.}$$

Hence mol-fraction of $O_2 = \frac{1}{8}$, mol-fraction of $H_2 = \frac{7}{8}$.

$$\therefore \text{The entropy-change} = -\frac{1}{8} R \ln \frac{1}{8} - \frac{7}{8} R \ln \frac{7}{8} = 0.754 \text{ calories/degree.}$$

IV.36. Entropy and Probability. In statistical considerations, the thermodynamic probability of a system means the maximum number of different ways in which a system in a given state may exist. To illustrate, let us take a simple case.

Let there be four points p, q, r and s distributed in two cells x and y . The distribution may have five complexions (or macrostates), as

Cell x	4	3	2	1	0
Cell y	0	1	2	3	4

i.e., in all five possible states.

If we select any one of these states, say the distribution 2 and 2, then the possible ways of their distribution between the two cells would be,

Cell x	pq	pr	ps	qr	qs	rs
Cell y	rs	qs	qr	ps	pr	pq

(the internal arrangement within any cell is ignored.)

Hence there are as many as six different ways (or microstates) in the given state of the system. The thermodynamic probability is thus ascertained. When the number of points is large as in the case of molecules in a volume of gas, the magnitude of the thermodynamic probability also becomes enormous.

Now we know, a system left to itself passes into a state of equilibrium. This really means attainment of maximum chaos or disorder which occurs when the molecules are distributed in maximum possible ways, i.e., when the thermodynamic probability is maximum. In other words, the thermodynamic probability is a measure of the disorder in the system. But we have seen, in Sec. IV.33, that

entropy of the system is a measure of the molecular disorder. We are thus led to the conclusion that the entropy S of a system is related to its thermodynamic probability W (Boltzmann), as,

$$S = f(W)$$

Now suppose we have two systems A and B with entropies S_A and S_B and probabilities W_A and W_B . If the two systems are combined as one system then

$$\text{the total entropy,} \quad S = S_A + S_B$$

$$\text{and the net probability,} \quad W = W_A \times W_B$$

$$\text{Hence,} \quad S_A + S_B = f(W) = f(W_A \times W_B)$$

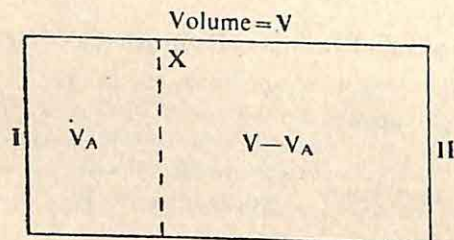
Such a relation is permitted only when S is a logarithmic function of W .

Planck suggested that the entropy should be related to the probability as

$$S = k \ln W \quad \dots \text{(IV.51)}$$

where k is the Boltzmann constant and equal to R/N_0 .

Now, let us take a rectangular box of volume V with a partition wall X which may be placed anywhere within so as to divide the box into two parts, V_A and $(V - V_A)$. Suppose that there is a single molecule of an ideal gas present in the box. The probability of the molecule to be found in the volume V_A at any given instant is obviously V_A/V . Then,



if the partition-wall coincides with the boundary I (i.e., $V_A = 0$) the probability will also be zero ;

if the partition-wall be at the middle (i.e., $V_A = V/2$), the probability would be $\frac{1}{2}$;

if the partition-wall coincides with the boundary II (i.e., $V_A = V$), then the probability would be one, i.e., a certainty.

If the box contain two molecules instead of one, the probability of finding both the molecules in V_A would be $(V_A/V)^2$ and if there be p molecules in the box, the probability is $(V_A/V)^p$.

Now suppose we take a gm.-mole of a perfect gas in the box, the probability of having all the molecules in V_A is

$$W_A = \left(\frac{V_A}{V} \right)^{N_0}, \text{ where } N_0 = \text{Avogadro number.}$$

In such a case if the partition be removed altogether, the probability of finding all the molecules in volume V is unity, i.e., $W = 1$.

$$\text{Hence} \quad \frac{W_A}{W} = \left(\frac{V_A}{V} \right)^{N_0}, \text{ or } \ln \frac{W_A}{W} = N_0 \ln \frac{V_A}{V}$$

or multiplying both sides by Boltzmann constant, k

$$k \ln \frac{W_A}{W} = k N_0 \ln \frac{V_A}{V} = R \ln \frac{V_A}{V}$$

If S_A and S denote the entropy of the gas in volume V_A and V , then applying equation (IV.51), we have

$$\begin{aligned} \Delta S &= S - S_A = k \ln W - k \ln W_A \\ &= -k \ln \frac{W_A}{W} \end{aligned}$$

$$\therefore \Delta S = R \ln \frac{V}{V_A}$$

This is exactly the entropy-change in the expansion of a gas from volume V_A to V , as deduced previously in Sec. IV.34. It, therefore, justifies the proposed relation between entropy and probability,

$$S = k \ln W.$$

FREE ENERGY FUNCTIONS : MAXWELL RELATIONS

Besides the parameters of a system (P, V, T), we have so far considered only three thermodynamic functions, namely, internal energy U , enthalpy H and entropy S . Two other functions which are very useful in various physical and chemical studies may now be introduced. These are free energy, F , and Gibbs potential or thermodynamic potential, G .

IV.37. Free Energy and Gibbs Potential. The two functions are defined as

$$F = U - TS \quad \dots \text{(IV.52)}$$

$$G = H - TS \quad \dots \text{(IV.53)}$$

We know that $\Delta Q = T\Delta S = T.(S_2 - S_1)$. This means that the product of temperature and entropy ($T \times S$) is a quantity of energy and as such it can be algebraically added to U or H .

Again, the magnitudes of U, H, S and T are defined by the states of the system. So, the values of F and G will also be defined by the states of the system. Further, dF and dG would be perfect differentials.

Since $H = U + PV$, we have also the relation,

$$G = U + PV - TS = F + PV \quad \dots \text{(IV.54)}$$

We can now make an attempt to understand the significance of these two functions, F and G . Suppose a system changes isothermally and reversibly from one state to another, then

$$F_i = U_i - TS_i$$

$$F_f = U_f - TS_f$$

the subscripts i and f denote initial and final states. Then

$$\Delta F_T = (U_f - U_i) - T.(S_f - S_i) = \Delta U - T.\Delta S.$$

When the process is reversible, $T\Delta S = \Delta Q$

$$\therefore \Delta F_T = \Delta U - T\Delta S = \Delta U - \Delta Q = -\Delta W \quad \dots \text{(IV.55)}$$

$$\text{or,} \quad -\Delta F_T = \Delta W,$$

where ΔW is the reversible (hence, maximum) work done by the system.

We can thus say that the thermodynamic function, *free energy* F , is such that its decrease gives the maximum amount of work available during an isothermal change of the system from one given state to another.

We must however remember that

(a) if the change be not isothermal, even then free energy will change but will not be equivalent to the maximum work.

(b) in the case of an irreversible change, the value of $-\Delta F$ will be the same as in a reversible change but the drop in free energy would exceed the output of work, i.e., $-\Delta F > \Delta W$.

(c) the decrease of the free energy ($-\Delta F$) would be equal to the total yield of work, which may be mechanical or otherwise or partly mechanical and partly otherwise.

The other function, Gibbs potential G , may also be treated similarly,

$$G = U + PV - TS$$

If a system undergoes an isothermal reversible change at a constant pressure, from one given state to another, then

$$\Delta G_{P,T} = \Delta U + P.\Delta V - T.\Delta S = P.\Delta V - \Delta W$$

$$\text{or,} \quad -\Delta G_{P,T} = \Delta W - P.\Delta V$$

The term $P.\Delta V$ denotes the mechanical work involved in the change of the system itself. Hence $(\Delta W - P.\Delta V)$ is the amount of work obtained exclusive of the mechanical work of the change of the system

We can then say that the Gibbs potential G is such a thermodynamic function that its decrease during an isothermal isobaric reversible process is equal to the network obtained.

$$-\Delta G = \Delta W - P\Delta V = \Delta W' \text{ (net non-mechanical work)} \quad \dots \text{ (IV.56)}$$

As in the previous case, this equality will not hold true in the case of an irreversible or a non-isothermal process.

Confusion in the Nomenclature : It is necessary to mention here the confusion that prevails in the literature of thermodynamics regarding the nomenclature of these two functions. The quantity ' $U - TS$ ' has been called free energy by one school of writers, while ' $H - TS$ ' has been named free energy by another school. In consequence, the subsequent derivations have been most confusing as the symbol F has been used differently by different schools. We mention here some of the expressions and symbols in use.

$U - TS$	$H - TS$
I. Work function, A	Free energy, F
II. Helmholtz function, A	Gibbs function, G
III. Free energy, F	Gibbs potential, G

We prefer to use in this book the last pair of names and symbols.

IV.38. Gibb's Helmholtz Relations. If a closed system undergoes a change, the only work involved being mechanical against the pressure, the infinitesimal reversible changes of F and G would be,

$$dF = dU - TdS - SdT = -PdV - SdT \quad \dots \text{ (IV.57)}$$

$$dG = dU + PdV + VdP - TdS - SdT = VdP - SdT \quad \dots \text{ (IV.58)}$$

Then, for an *isochoric* process :

$$dF_V = -SdT, \text{ or } \left(\frac{\partial F}{\partial T} \right)_V = -S \quad \dots \text{ (IV.59)}$$

$$\text{Hence, } F = U - TS = U + T \left(\frac{\partial F}{\partial T} \right)_V \quad \dots \text{ (IV.60)}$$

Again, for an *isobaric* process :

$$dG_P = -SdT, \text{ or } \left(\frac{\partial G}{\partial T} \right)_P = -S \quad \dots \text{ (IV.61)}$$

$$\text{Hence, } G = H - TS = H + T \left(\frac{\partial G}{\partial T} \right)_P \quad \dots \text{ (IV.62)}$$

These two equations (IV.60 and IV.62), which correlate free energy and Gibbs potential with internal energy or enthalpy are commonly known as Gibb's-Helmholtz relations. Such relations may also be derived in other forms.

Suppose a system undergoes a physical or a chemical change reversibly and isothermally from state I to state II. The states are specified by the function U_1, H_1, S_1, F_1, G_1 , and U_2, H_2, S_2, F_2, G_2 . The system has a definite mass in equilibrium with the external pressure.

$$\text{Then, } F_1 = U_1 - TS_1 \text{ and } F_2 = U_2 - TS_2$$

$$\therefore \Delta F = \Delta U - T\Delta S$$

$$\text{From eqn. (IV.59), } \Delta S = (S_2 - S_1)$$

$$= - \left[\left(\frac{\partial F_2}{\partial T} \right)_V - \left(\frac{\partial F_1}{\partial T} \right)_V \right] = - \left(\frac{\partial (\Delta F)}{\partial T} \right)_V \quad \dots \text{ (IV.63)}$$

$$\text{Substituting, } \Delta F = \Delta U + T \left(\frac{\partial (\Delta F)}{\partial T} \right)_V \quad \dots \text{ (IV.64)}$$

$$\text{Again, } G_1 = H_1 - TS_1 \text{ and } G_2 = H_2 - TS_2$$

$$\therefore \Delta G = \Delta H - T\Delta S$$

$$\text{From eqn. (IV.61), } \Delta S = (S_2 - S_1)$$

$$\text{or } \Delta S = - \left[\left(\frac{\partial G_2}{\partial T} \right)_P - \left(\frac{\partial G_1}{\partial T} \right)_P \right] = - \left(\frac{\partial(\Delta G)}{\partial T} \right)_P \quad \dots \text{ (IV.65)}$$

$$\text{Substituting, } \Delta G = \Delta H + T \left(\frac{\partial(\Delta G)}{\partial T} \right)_P \quad \dots \text{ (IV.66)}$$

The pair of equations, (IV.64) and (IV.66),

$$\left. \begin{aligned} \Delta F &= \Delta U + T \left[\frac{\partial(\Delta F)}{\partial T} \right]_V \\ \text{and } \Delta G &= \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_P \end{aligned} \right\} \quad \dots \text{ (IV.67)}$$

constitute another form of Gibb's-Helmholtz relations. These relations have very useful applications, especially in chemical processes, as will be seen in subsequent chapters.

IV.39. Maxwell's Relations. Derived from the definitions of thermodynamic functions, there are four relations, called Maxwell's relations, which are extensively used, particularly for systems in equilibrium. These can be arrived at in the following way.

$$\begin{aligned} \text{We know,} \quad & U, \text{ internal energy} \\ & H = U + PV \\ & F = U - TS \\ & G = H - TS \end{aligned}$$

Then,

$$\begin{aligned} (a) \quad dU &= dQ - dW = TdS - PdV \\ (b) \quad dH &= dU + PdV + VdP = TdS + VdP \\ (c) \quad dF &= dU - TdS - SdT = -PdV - SdT \\ (d) \quad dG &= dH - TdS - SdT = VdP - SdT \end{aligned}$$

Now, from (a) we have

$$\begin{aligned} (i) \quad \left(\frac{\partial U}{\partial S} \right)_V &= T, \quad \text{or} \quad \frac{\partial^2 U}{\partial S \partial V} = \left(\frac{\partial T}{\partial V} \right)_S \\ (ii) \quad \left(\frac{\partial U}{\partial V} \right)_S &= -P, \quad \text{or} \quad \frac{\partial^2 U}{\partial V \partial S} = - \left(\frac{\partial P}{\partial S} \right)_V \end{aligned}$$

Since dU is a perfect differential, so,

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \dots \text{ (A)}$$

Again from (b), we find

$$\begin{aligned} (i) \quad \left(\frac{\partial H}{\partial S} \right)_P &= T, \quad \text{or} \quad \frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial T}{\partial P} \right)_S \\ (ii) \quad \left(\frac{\partial H}{\partial P} \right)_S &= V, \quad \text{or} \quad \frac{\partial^2 H}{\partial P \partial S} = \left(\frac{\partial V}{\partial S} \right)_P \end{aligned}$$

$$\text{Hence,} \quad \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \quad \dots \text{ (B)}$$

Then from (c), we have

$$\begin{aligned} (i) \quad \left(\frac{\partial F}{\partial V} \right)_T &= -P, \quad \text{or} \quad \frac{\partial^2 F}{\partial V \partial T} = - \left(\frac{\partial P}{\partial T} \right)_V \\ (ii) \quad \left(\frac{\partial F}{\partial T} \right)_V &= -S, \quad \text{or} \quad \frac{\partial^2 F}{\partial T \partial V} = - \left(\frac{\partial S}{\partial V} \right)_T \end{aligned}$$

Hence,

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad \dots (C)$$

Further from (d), we find

$$\begin{aligned} (i) \quad \left(\frac{\partial G}{\partial P}\right)_T &= V, \quad \text{or} \quad \frac{\partial^2 G}{\partial P \partial T} = \left(\frac{\partial V}{\partial T}\right)_P \\ (ii) \quad \left(\frac{\partial G}{\partial T}\right)_P &= -S, \quad \text{or} \quad \frac{\partial^2 G}{\partial T \partial P} = -\left(\frac{\partial S}{\partial P}\right)_T \end{aligned}$$

So,

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad \dots (D)$$

The four relations A, B, C and D, grouped together, are

$$\left. \begin{aligned} (i) \quad \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\ (ii) \quad \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\ (iii) \quad \left(\frac{\partial P}{\partial T}\right)_V &= \left(\frac{\partial S}{\partial V}\right)_T \\ (iv) \quad \left(\frac{\partial V}{\partial T}\right)_P &= -\left(\frac{\partial S}{\partial P}\right)_T \end{aligned} \right\} \quad \dots (IV.68)$$

IV.40. Criteria of Spontaneity and Conditions of Equilibrium. In a reversible change, we have seen, the entropy remains unaltered, while if the change be spontaneous and hence irreversible, the entropy is increased. So,

$$\begin{aligned} (a) \quad \text{for a reversible change,} \quad \Sigma dS &= 0 \\ (b) \quad \text{for an irreversible change,} \quad \Sigma dS &> 0 \end{aligned}$$

Now let us consider a system with its surroundings. If an *isothermal* process occurs in such a system, there must also occur heat or work transfer between the system and the surroundings. Let dS and dS' be the entropy-changes in the system and surroundings respectively. Therefore,

$$\begin{aligned} (a) \quad \text{when the change is reversible} \quad dS + dS' &= 0 \\ (b) \quad \text{when the change is irreversible} \quad dS + dS' &> 0 \end{aligned}$$

Combining the two, we may write, $dS + dS' \geq 0$

If we further regard the change in the surroundings as reversible and suppose

the surroundings supply heat dQ reversibly, then $dS' = -\frac{dQ}{T}$

If dU be the internal energy increase of the system and ΔW be the work done by the system, then from the first law,

$$dS' = -\frac{dU + \Delta W}{T}$$

Now,

$$dS + dS' \geq 0$$

i.e.,

$$dS - \frac{dU + \Delta W}{T} \geq 0$$

or

$$TdS - dU - \Delta W \geq 0 \quad \dots (A)$$

We must remember that the symbols in this equation refer to the system only. We find,

$$(i) \quad \text{for a real process to occur in nature, } TdS - dU - \Delta W > 0 \quad \dots (B)$$

(ii) for bringing about an infinitesimal reversible change of the system,

$$TdS - dU - \Delta W = 0 \quad \dots (C)$$

A system may be said to be in equilibrium when its state does not change in any way with time. Any virtual infinitesimal change imagined with a system in equilibrium would be a reversible one. We can then assert that for a system in equilibrium, the condition (C) would be valid. In other words a system in which all conceivable virtual changes satisfy the equation (C) must be stable *i.e.*, in equilibrium.

We can now attempt to simplify this relation by imposing certain restraints. Suppose the work done is mechanical (*i.e.*, $\Delta W = PdV$), then we can rewrite the equation, (A) as,

$$TdS - dU - PdV \geq 0 \quad \dots (D)$$

(a) Now if U and V be constant, then

$$dS_{U,V} \geq 0$$

The inequality sign is for real changes and the equality sign refers to the condition of equilibrium. We know entropy goes on increasing as equilibrium is approached. Hence, at equilibrium, S becomes maximum and $dS_{U,V} = 0$

(b) We know $dF = dU - TdS - SdT$

Substituting this in equation (D), we have

$$-dF - SdT - PdV \geq 0$$

$$\text{or} \quad dF \leq -SdT - PdV$$

In an *isothermal* process, if the system yields *no work*,

$$\text{then} \quad dF \leq 0.$$

That is, in a real process $dF < 0$, *i.e.*, free energy diminishes. When equilibrium is reached free energy becomes minimum. We can write,

(i) for a spontaneous change, $dF_{V,T} < 0$

(ii) for equilibrium state, $dF_{V,T} = 0$

(c) We know $dG = dU + PdV + VdP - SdT - TdS$

Substituting this in equation (D), we have

$$-dG + VdP - SdT \geq 0$$

$$\text{or} \quad dG \leq VdP - SdT$$

At *constant pressure* in an *isothermal process*,

$$dG \leq 0$$

That is, in a real process $dG < 0$ or Gibbs potential diminishes. When equilibrium is reached, Gibbs potential is minimum. We can say,

(i) for a spontaneous change, $dG_{P,T} < 0$

(ii) for equilibrium state, $dG_{P,T} = 0$

The criterion of equilibrium is thus,

$$\left. \begin{aligned} dS_{U,V} &= 0 \\ dF_{V,T} &= 0 \\ dG_{P,T} &= 0 \end{aligned} \right\} \quad \dots (IV.69)$$

The possibility of a chemical change

For a process taking place from a given initial to a final state, ΔU must be the same. From the 1st law,

for the reversible occurrence, $\Delta q_{\text{rev}} = \Delta U + \Delta W_{\text{rev}}$
and for the irreversible occurrence, $\Delta q_{\text{irrev}} = \Delta U + \Delta W_{\text{irrev}}$

We have also seen, $\Delta W_{\text{rev}} > \Delta W_{\text{irrev}}$, hence $\Delta q_{\text{rev}} > \Delta q_{\text{irrev}}$

or, for an infinitesimal change, $dq_{\text{rev}} > dq_{\text{irrev}}$

$$\text{i.e., } dq_{\text{irrev}} - dq_{\text{rev}} < 0 \quad \dots (A)$$

Now, by definition, $G = H - TS = U + PV - TS$

$$\text{or } dG_T = dU + PdV + VdP - TdS$$

$$\text{or } dG_T = dq - dW + PdV + VdP - TdS$$

Supposing that the work involved is mechanical *i.e.*, measured in pressure-volume changes, then $dW = PdV$

$$\text{or } dG_T = dq + VdP - TdS$$

Chemical reactions are often carried out at constant temperature and also mostly at constant pressure, hence

$$dG_{P,T} = dq - TdS$$

Now, the spontaneous process would occur in an irreversible fashion, so

$$dG_{P,T} = dq_{\text{irrev}} - TdS = dq_{\text{irrev}} - dq_{\text{rev}}$$

[For, by definition, $dS = dq_{\text{rev}}/T$]

Then, from (A) above, $dG_{P,T} < 0$.

That is, for a process to occur spontaneously, $dG_{P,T} < 0$. In other words, Gibbs potential change (ΔG) shall be negative in a spontaneous process. Every system tends to attain equilibrium, so G will diminish gradually and at equilibrium it will attain the minimum value, *i.e.*, $dG_{P,T} = 0$

$\therefore$ For a spontaneous process, $dG_{P,T} < 0$

and at equilibrium, $dG_{P,T} = 0$.

The possibility of the spontaneous occurrence of a chemical process is determined by ascertaining whether the Gibbs potential change (ΔG) is negative for the change under the given conditions. Since

$$\Delta G = \Delta H - T\Delta S, \quad \dots (B)$$

the Gibbs potential change can be determined if we can find out the change in enthalpy (ΔH) and the change in entropy (ΔS) for the reaction.

The enthalpy change (ΔH) is obtained from the measurement of the heat of reaction or may be computed from the bond energies in the molecules of reactants and products.

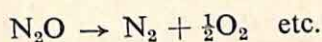
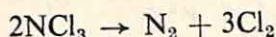
The entropy-change (ΔS) is available from the individual entropies of the reactants and the resultants or from other measurements such as e.m.f. etc. The entropy increases whenever as a result of the reaction the randomness or the extent of disorder increases. It is generally true that when a solid reactant gives gaseous products, the entropy increases, *i.e.*, ΔS is positive. Similarly in gaseous reactions also, the sign of the entropy-change is determined from the number of resultant and reactant molecules. If the number of product molecules be larger, ΔS will be positive. Evidently all dissociation processes are attended with an increase in entropy.

The variation of entropy-change with temperature and also the variation of enthalpy-change with temperature are not very large. Hence for approximate estimations, ΔH and ΔS determined at a convenient temperature may be used for reactions at other temperatures without an appreciable error. But the change in Gibbs potential (ΔG) varies considerably with temperature.

From eqn (B) it is evident (i) the more negative ΔH is the more negative is ΔG and (ii) the more positive ΔS is the more negative is ΔG . This shows that systems at constant pressure and temperature would try to move to a state of maximum entropy and minimum enthalpy.

In processes where ΔH is negative and ΔS is positive, we have negative values for ΔG . Such processes would occur spontaneously. Many dissociations come in this category :

$$\Delta H = -ve, \Delta S = +ve,$$



Thus, ΔH for dissociation of N_2O is -20000 cal and $\Delta S = 18$ cal/degree. Hence, at 25°C ,

$\Delta G = -20000 - 298 \times 18 = -25364$ cals. The dissociation would be spontaneous.

In endothermic reactions, ΔH is positive. The reactions will proceed if $T\Delta S$ is positive and greater than ΔH . For example, in the water-gas reaction,



the entropy increases, as the reactant C has least disorder, $\Delta S = 32$ cal/degree.

The enthalpy change was found to be $+31400$ cal. Hence, at 25°C ,

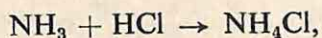
$$\Delta G = 31400 - 32 \times 298 = +21864 \text{ cal}$$

But if the temperature be high, say 1200°K , then

$$\Delta G = 31400 - 32 \times 1200 = -7000 \text{ cal}$$

Therefore, the reaction will not occur at 298°K but will be spontaneous at 1200°K . Incidentally this shows the profound influence of temperature on ΔG .

Similarly, in reactions where ΔH is negative and ΔS is also negative, the process will be spontaneous if only ΔH is numerically greater than $T\Delta S$. Say, in the reaction,



ΔH is negative and greater than $T\Delta S$ at ordinary temperature. Hence, the reaction. But at high temperatures, $T\Delta S$ exceeds ΔH and so dissociation of ammonium chloride would occur.

SOME SIMPLE APPLICATIONS OF THE THERMODYNAMIC LAWS

I. HEAT CAPACITY RELATIONS

IV.41. Variation of Heat Capacities with Pressure and Volume :

(i) C_V with V .

$$\text{We know, } C_V = \left(\frac{\partial q}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V, \text{ or, } \frac{\partial C_V}{\partial V} = T \frac{\partial^2 S}{\partial T \partial V}$$

From Maxwell relations,

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \quad \text{or,} \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{\partial^2 S}{\partial V \partial T}$$

Hence,

$$\frac{\partial C_V}{\partial V} = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

For an ideal gas, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$, and $\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$.

$$\therefore \frac{\partial C_V}{\partial V} (\text{ideal gas}) = 0.$$

For a real gas (van der Waals), $\left(P + \frac{a}{V^2}\right)(V-b) = RT$.

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}, \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0.$$

For a real gas, therefore, $\frac{\partial C_V}{\partial V} = 0$.

(ii) C_P with P .

We know, $C_P = T \left(\frac{\partial S}{\partial T}\right)_P \quad \therefore \quad \frac{\partial C_P}{\partial P} = T \frac{\partial^2 S}{\partial T \partial P}$

From Maxwell's relations, $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$, or, $\left(\frac{\partial^2 V}{\partial T^2}\right)_P = -\frac{\partial^2 S}{\partial P \partial T}$

$$\therefore \frac{\partial C_P}{\partial P} = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

For an ideal gas, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$, and $\left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0$.

$$\therefore \frac{\partial C_P}{\partial P} (\text{ideal gas}) = 0.$$

For a real gas (van der Waals),

$$RT = PV - Pb + \frac{a}{V} - \frac{ab}{V^2} \approx PV - Pb + \frac{a}{V}.$$

$$\therefore \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - \frac{a}{V^2}}.$$

Then,
$$\begin{aligned} \left[\frac{\partial^2 V}{\partial T^2}\right]_P &= -\frac{R}{\left[P - \frac{a}{V^2}\right]^2} \times \frac{2a}{V^3} \times \left(\frac{\partial V}{\partial T}\right)_P \\ &= -\frac{R}{\left[P - \frac{a}{V^2}\right]^2} \times \frac{2a}{V^3} \times \frac{R}{\left[P - \frac{a}{V^2}\right]} = -\frac{2aR^2}{P^3 V^3 \left[1 - \frac{a}{PV^2}\right]^3} \\ &\approx \frac{-2aR^2}{R^3 T^3 \left[1 - \frac{a}{RTV}\right]^3} = -\frac{2a}{RT^3} \left[1 + \frac{3a}{RTV}\right] \end{aligned}$$

Neglecting the second term, on first approximation,

$$\frac{\partial C_P}{\partial P} = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P = \frac{2a}{RT^2} \quad \dots (IV.70)$$

Problem : What would be the change in the C_P -value of oxygen when at 27°C , its pressure is increased from zero to 50 atmospheres, supposing it behaves as a van der Waals' gas. Given $a = 1.36 \text{ litre}^2\text{-atm}$.

$$\begin{aligned} C_P - C_{P_0} &= \Delta C_P = \int_0^P \frac{2a}{RT^2} dP = \frac{2a}{RT^2} P. \\ &= \frac{2 \times 1.36 \times 50}{(.082) \times 300^2} \times 24.2 \text{ calories per degree per mole} \\ &= 0.44 \text{ cal/degree-mole} \quad (1 \text{ litre-atm.} = 24.2 \text{ cal}). \end{aligned}$$

IV.42. Heat-capacity Difference, $C_P - C_V$.

We have,
$$dq = \left(\frac{\partial q}{\partial V} \right)_T dV + \left(\frac{\partial q}{\partial T} \right)_V dT = T \left(\frac{\partial S}{\partial V} \right)_T dV + C_V dT$$

or
$$\left(\frac{\partial q}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + C_V$$

or
$$C_P - C_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \quad \dots (IV.71)$$

Applying Maxwell relation,

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \quad \dots (IV.72)$$

Since $\left(\frac{\partial P}{\partial T} \right)_V$ and $\left(\frac{\partial V}{\partial T} \right)_P$ are usually positive, C_P is generally greater than C_V in any system. At 0°K , however, $C_P = C_V$. Besides, when $\left(\frac{\partial V}{\partial T} \right)_P \rightarrow 0$, as in water at 4°C , $C_P \rightarrow C_V$.

(i) In an ideal gas, $\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$, and $\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V}$.

Hence,
$$C_P - C_V = T \frac{R}{P} \cdot \frac{R}{V} = R.$$

(ii) In a van der Waals gas, $\left(P + \frac{a}{V^2} \right) = \frac{RT}{V-b}$.

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b}; \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P - \frac{a}{V^2}} \quad (\text{Sec. IV.41})$$

Hence,
$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = T \cdot \frac{R}{V-b} \cdot \frac{R}{P - \frac{a}{V^2}}$$

$$= \frac{RT}{V-b} \cdot \frac{R}{\left(P + \frac{a}{V^2} \right) - \frac{2a}{V^2}} = \frac{RT}{V-b} \cdot \frac{R}{\frac{RT}{V-b} - \frac{2a}{V^2}}$$

$$= \frac{RT}{V-b} \cdot \frac{RT}{V-b} \left[1 - \frac{2a(V-b)}{RTV^2} \right] \approx R \left[1 + \frac{2a}{RTV} \right] - R \left[1 + \frac{2aP}{R^2T^2} \right] \dots (IV.73)$$

(b) Since $V = f(P, T)$,

we have,
$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

For a change at constant volume, $\left(\frac{\partial V}{\partial P} \right)_T dP = - \left(\frac{\partial V}{\partial T} \right)_P dT$

or
$$\left(\frac{\partial V}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V = - \left(\frac{\partial V}{\partial T} \right)_P$$

or
$$\left(\frac{\partial P}{\partial T} \right)_V = - \left(\frac{\partial V}{\partial T} \right)_P / \left(\frac{\partial V}{\partial P} \right)_T$$

Substituting this in equation (IV.72),

$$C_P - C_V = -T \left(\frac{\partial V}{\partial T} \right)_P^2 / \left(\frac{\partial V}{\partial P} \right)_T = -T \cdot \frac{\frac{1}{V^2} \left(\frac{\partial V}{\partial T} \right)_P^2}{\frac{1}{V^2} \left(\frac{\partial V}{\partial P} \right)_T}$$

or
$$C_P - C_V = -T \frac{\alpha^2}{-\beta/V} = \frac{\alpha^2 VT}{\beta} \dots (IV.74)$$

where α and β signify the usual coefficients of expansion and of compressibility. This relation is particularly useful for dealing with condensed systems (eqn I.19 & 20).

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \text{ and } \beta = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

Problem : Find out $(C_P - C_V)$ value of decane at 27°C , given molar volume 106 c.c. ; the coefficient of expansion $\alpha = 1 \times 10^{-3}$, and coefficient of compressibility $\beta = 106 \times 10^{-6} \text{ atm.}^{-1}$.

$$\begin{aligned} C_P - C_V &= \frac{\alpha^2 VT}{\beta} = \frac{(1 \times 10^{-3})^2 \times 106 \times 300}{106 \times 10^{-6}} \text{ c.c.-atm.} \\ &= 300 \times .0242 = 7.26 \text{ calories} \end{aligned}$$

II. JOULE-THOMSON EFFECT

IV.43. Joule-Thomson Coefficient. Joule's experiment, (Sec. IV.11) in free expansion of a gas into a vacuum revealed that the temperature-drop of the system was negligible and would be zero if the gas were ideal. But Joule and Thomson's subsequent experiments on the passage of a gas from a higher pressure to a lower one through fine orifices of a porous plug revealed a drop in temperature in many cases.

Suppose the volume V_1 of a gas under a constant pressure P_1 is allowed to pass through a porous barrier from the region on the left to the region on the right where the constant pressure is P_2 .

The volume of the gas becomes V_2 . The process is made reversible with the slow motion of the two frictionless pistons at the two ends (Fig. IV.22). The whole system is thermally insulated, such that $dQ = 0$.

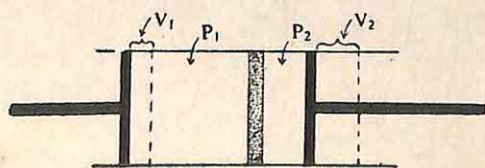


FIG. IV.22

The work done by the piston on the left $= P_1 V_1$.

The work obtained from the system on the right $= P_2 V_2$

Then, from the first law, $\Delta U = -\Delta W = P_1 V_1 - P_2 V_2$

or $U_2 - U_1 = P_1 V_1 - P_2 V_2$

or $U_1 + P_1 V_1 = U_2 + P_2 V_2$

or $H_1 = H_2$

or $\Delta H = 0$

This means that in the adiabatic expansion of a gas through fine orifices the heat-content remains unaltered. That is, such adiabatic expansion is also *isoenthalpic*. Nevertheless there is a drop of temperature generally of the outcoming gas and such variation of temperature is called *Joule-Thomson effect*.

The rate of change in temperature with pressure when enthalpy remains constant is called *Joule-Thomson Coefficient*,

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H \quad \dots (IV.75)$$

In such flow through fine orifices, usually the gas runs into lower pressures, i.e., dP is negative. Hence μ will be positive if dT also is negative, i.e., if temperature falls. At ordinary temperatures, most gases cool down in passing to lower pressures through porous plugs. Hydrogen and Helium, however, at room temperatures become heated instead of cooling, i.e., μ is negative. We can explain this in the following way. We know,

$$dH = \left(\frac{\partial H}{\partial P} \right)_T dP + \left(\frac{\partial H}{\partial T} \right)_P dT$$

In an isoenthalpic change like the above, $dH = 0$,

$$\therefore \left(\frac{\partial H}{\partial T} \right)_P dT = - \left(\frac{\partial H}{\partial P} \right)_T dP$$

$$\text{or} \quad \left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\partial H}{\partial P} \right)_T / \left(\frac{\partial H}{\partial T} \right)_P = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T$$

$$\text{or} \quad \mu = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T \quad \dots (IV.76)$$

$$\text{Since } H = U + PV; \mu = - \frac{1}{C_P} \left(\frac{\partial U}{\partial P} \right)_T - \frac{1}{C_P} \left(\frac{\partial(PV)}{\partial P} \right)_T \quad \dots (IV.77)$$

This relation is obviously applicable both to ideal and also to real gases. In the case of an ideal gas, both the terms on the right-hand side separately vanish,

for $\left[\frac{\partial U}{\partial P} \right]_T = 0$, and $\left[\frac{\partial(PV)}{\partial P} \right]_T = 0$, hence $\mu = 0$.

The case of a real gas is different. We can re-write equation (IV.77) as

$$\mu = - \frac{1}{C_P} \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial P} \right)_T - \frac{1}{C_P} \left[\frac{\partial(PV)}{\partial P} \right]_T \quad \dots (IV.77a)$$

In this equation, $\left(\frac{\partial U}{\partial V} \right)_T$ of gas is usually positive, while $\left(\frac{\partial V}{\partial P} \right)_T$ for any gas is always negative. As a result, the first term is always positive. The magnitude of the second term $\left[\frac{\partial(PV)}{\partial P} \right]_T$ may be negative or may be positive. At low temperatures and at low pressures, $\left[\frac{\partial(PV)}{\partial P} \right]_T$ is negative. Under such conditions both the

terms in the equation being positive, μ has a positive value. That means that there would be a cooling of the gas. Even at ordinary temperatures, except for Hydrogen and Helium, all other gases show $\left[\frac{\partial(PV)}{\partial P} \right]_T$ negative at lower pressures.

But at higher pressures $\left[\frac{\partial(PV)}{\partial P} \right]_T$ becomes positive so that second term becomes negative and if its value exceeds that of the first term, μ becomes negative.

At high temperatures all gases have $\left[\frac{\partial(PV)}{\partial P} \right]_T$ positive, so μ is generally negative.

The cooling effect is observed at relatively low temperatures but if the temperature be high, then instead of cooling the gases become heated, *i.e.*, J-T effect μ becomes negative. For every gas there is a temperature where $\mu = 0$, when neither heating nor cooling of the gas due to passage through fine orifices would occur. This is called the 'inversion temperature T_i ' of the gas.

We shall first attempt to find a useful expression for μ . We have

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP$$

(from IV.68)

$$= \frac{C_P}{T} dT + \left(\frac{\partial S}{\partial P} \right)_T dP = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

Now

$$dH = dU + PdV + VdP = TdS + VdP$$

Substituting dS in this relation,

$$dH = T \left[\frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP \right] + VdP$$

In an isoenthalpic change, $dH = 0$, hence

$$\begin{aligned} C_P dT_H &= T \left(\frac{\partial V}{\partial T} \right)_P dP - VdP \\ &= \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] dP \end{aligned}$$

or

$$\left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \quad \dots (IV.79)$$

For a van der Waals' gas, we know

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P - \frac{a}{V^2}} = \frac{R}{\left(P + \frac{a}{V^2} \right) - \frac{2a}{V^2}} = \frac{R}{\frac{RT}{V-b} - \frac{2a}{V^2}}$$

So,

$$T \left(\frac{\partial V}{\partial T} \right)_P - V = \frac{RT}{\frac{RT}{V-b} - \frac{2a}{V^2}} - V = \frac{(V-b)}{1 - \frac{2a(V-b)}{RTV^2}} - V$$

$$\approx (V-b) \left[1 + \frac{2a(V-b)}{RTV^2} \right] - V$$

$$= \frac{2a(V-b)^2}{RTV^2} - b \approx \frac{2a}{RT} - b.$$

Substituting this in equation (IV.79), the Joule-Thomson effect,

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_P} \left[\frac{2a}{RT} - b \right] \quad \dots (IV.80)$$

The knowledge of heat-capacity and the van der Waals' constants would enable us to evaluate the Joule-Thomson effect at a given temperature T .

At high temperatures $\frac{2a}{RT} < b$, hence μ is negative. At low temperatures $\frac{2a}{RT} > b$, hence μ is positive. For Hydrogen, where 'a' is small, $\frac{2a}{RT}$ even for ordinary temperatures is less than 'b', so there is heating in Joule-Thomson expansion. It must be remembered that in the adiabatic expansion of a gas, there is always a cooling effect due to the decrease in the int. energy in the performance of work. But in Joule-Thomson effect, cooling will occur only when μ is positive.

Putting $\mu = 0$, at the inversion temperature T_i , we have

$$\frac{2a}{RT_i} - b = 0,$$

or,

$$T_i = \frac{2a}{Rb} \quad \dots (IV.81)$$

IV.44. Liquefaction of Gases. Systematic researches in liquefaction of gases began from 1823 when Faraday succeeded in liquefying all gases which require moderate pressure and moderately low temperature for condensation. Some earlier workers, however, liquefied gases like ammonia, sulphur dioxide, chlorine, etc., either by cooling alone or by compression. Faraday's simple method consisted of heating a solid kept at one end of a sealed inverted V-tube, the other end being kept immersed in a freezing mixture (Fig. IV.23). Though most of the common gases could

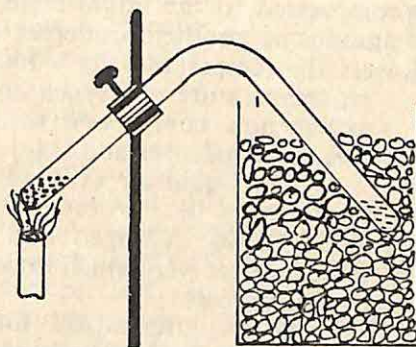


FIG. IV.23. Faraday's liquefaction of chlorine

be liquefied by this method, gases like Hydrogen, Nitrogen, Oxygen, etc., resisted all attempts at liquefaction. These were then named permanent gases. Meantime, Andrews experiments furnished the existence of *critical temperature* above which liquefaction is impossible. Moreover, the discovery of Joule-Thomson cooling effect provided another valuable means of attainment of very low temperature.

The following steps are taken in the liquefaction of gases : (i) the gas must be below its critical temperature ; (ii) the pressure must be sufficiently high, the lower the temperature less is the required pressure ; (iii) the gas is cooled by Joule-Thomson adiabatic expansion ; (iv) it is also cooled by performance of external work in an engine and (v) the incoming gas is lowered in temperature by the outgoing gas already cooled by expansion.

In the earlier days, some so called permanent gases were liquefied by the *method of cascades*. The applicability of this method rests on the fact that by evaporation of a liquid under reduced pressure, sufficiently low temperature, which is below the critical temperature of the gas to be liquefied, can be attained.

The method was first employed by R. Pictet (1878). As a very good example, the liquefaction of oxygen by K. Onnes (1894) may be cited. Methyl chloride (cr. temp. 143°C) was easily liquefied at room temperature by application of pressure. The liquid methyl chloride was then allowed to flow through the jacket of a condenser (Fig. IV.24), under a reduced pressure and allowed to evaporate lowering

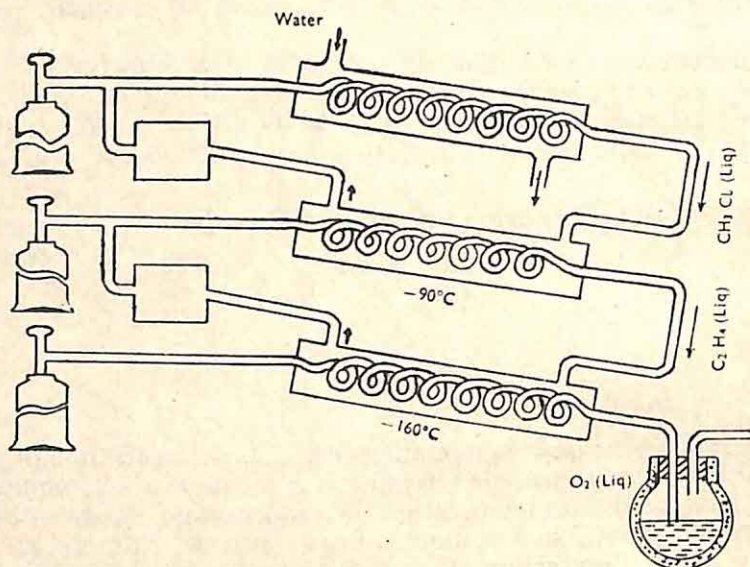


FIG. IV.24

the temperature to -90°C . Ethylene gas is made to pass through the inner tube of the condenser and is compressed to the liquid state. The liquid ethylene is made to pass through the annulus of another condenser under reduced pressure where it vaporises and lowers the temperature to -160°C , which is below the cr. temperature of oxygen and nitrogen. Oxygen (or air) is now compressed through the inner tube of this last condenser and is liquefied.

The liquid air evaporation under reduced pressure gave the lowest attainable temperature of -218°C . So hydrogen and helium, whose critical temperatures were much lower, could not be liquefied by this process.

Soon afterwards, Linde in Germany and Hampson in England employed Joule-Thomson effect to produce cooling. The operating principle of Linde process is indicated in Fig. IV.25. The gas is compressed in a pump (A) and passed through coil (B) immersed in a refrigerant like liquid ammonia and then after further cooling in C, it is forced through a small opening E, when it falls to atmospheric pressure. Such a J-T adiabatic expansion by itself does not cause much lowering. For example, air at 20°C by falling from 50 to 1 atmosphere suffers a temperature-drop of 12° only. The temperature-drop may be increased if the gas already cooled is circulated round the incoming gas, and this further cooled incoming gas undergoes a J-T expansion producing a still lower temperature. Repetition of this leads to cumulative cooling effect and the gas finally reaches its liquefying temperature. The lower the initial temperature, the greater is the magnitude of temperature-drop in J-T expansion. The process is indeed one of regenerative cooling.

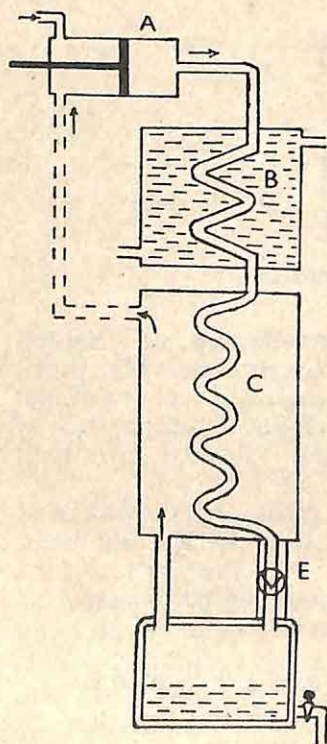


FIG. IV.25

The Linde process, though extensively used, is not a very efficient one. Instead of wasting the energy of compression by free expansion to atmosphere as in Linde process, the Claude process conserves a portion of it by passing a large fraction of the gas through an engine X in Fig. IV.26. The work done by the engine helps to operate the compressor (A) and the power consumption is reduced. In the performance of the work in X , the gas itself gets cooled to a considerable extent. The rest of the process is the same as in Linde's.

The liquefaction of hydrogen and helium proved very difficult due to (i) their intermolecular forces being very small and (ii) their inversion temperatures and the critical temperatures being very low. Dewar (1898) succeeded in liquefying hydrogen for the first time by applying Linde's principle of regenerative cooling and using liquid air (evaporating under reduced pressure) as refrigerating agent, when a temperature of -200°C was reached. The gas was then made to suffer J-T expansion through a nozzle E . After a few operations, the gas liquefied. Kammerling Onnes (1908) liquefied helium following a similar process and precooling the gas with liquid hydrogen. Helium has a cr. temperature of 5.25°K and indeed Onnes succeeded in reaching as low a temperature as 0.82°K . Kapitza (1934) liquefied both hydrogen and helium by using his 'expansion engine' with loose pistons without lubricants.

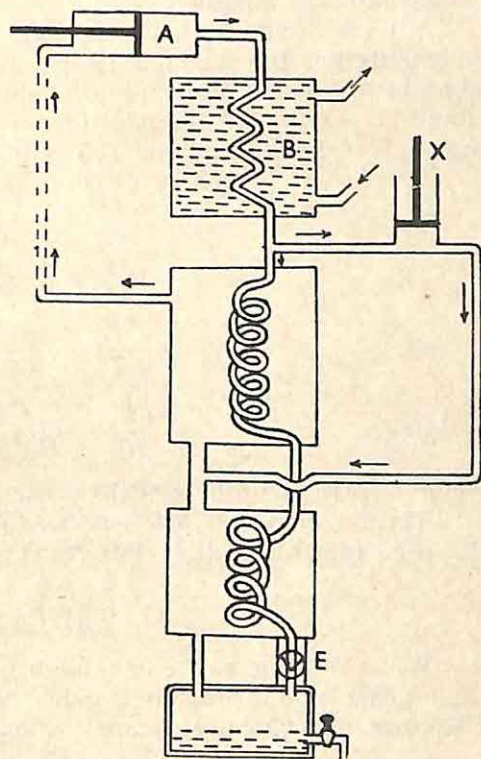


FIG. IV.26

When Helium was solidified (Keesom, 1926), the attention of the physicists was concentrated on the attainment of still lower temperature. The race towards unattainable zero degree absolute was rendered possible by the discovery of a new principle called *adiabatic demagnetisation* of paramagnetic salts first suggested by Debye and by Giauque independently in 1926.

Adiabatic Demagnetisation. The entropy of a paramagnetic substance arises partly out of thermal and partly out of magnetic properties. If such a substance is placed in a magnetic field, the atomic dipoles take up or tend to take up a definite pattern according to the direction of the field. This arrangement in a definite pattern leads to a decrease in entropy. If the substance is now thermally insulated and the magnetic field be removed *adiabatically*, the entropy will not change as the adiabatic changes are isoentropic. On demagnetisation, atomic dipoles distribute randomly causing an increase in magnetic entropy. Since total entropy is constant, there will be drop in thermal entropy, and there would be a fall in temperature. Such cooling by adiabatic demagnetisation is appreciable only when the temperature is extremely low, as only in such conditions magnetic entropy approaches the range of thermal entropy. In fact, paramagnetic substances like Gadolinium sulphate, ferric ammonium alum etc., are first cooled to 1°K by means of evaporating liquid helium. A magnetic field of 30000 gauss is applied. The rise in temperature is counteracted by the conducting gas. When the original temperature is reached, the gas is pumped out and the salt thermally insulated. The field is then switched off and the temperature drops. The lowest temperature reached by this process is 0.003°K .

III. CHANGE OF PHASE : CLAPEYRON EQUATION

IV.45. Clapeyron Equation. Another simple application of the thermodynamic relations is in the study of change of phase of substances, such as freezing, vaporisation etc. We shall first consider the variation of pressure with temperature in the vaporisation of a liquid.

(a) Let G_1 and G_2 be the Gibbs potentials of a liquid and its vapour which are in equilibrium in a system at temperature T . Imagine a virtual change of a small amount of liquid vaporising at equilibrium. The drop in Gibbs potential of the liquid is $-\Delta G_1$ and the gain in the same for the vapour is $+\Delta G_2$. Since the system is in equilibrium, net $\Delta G = 0$, (eqn. IV.69).

$$\therefore -\Delta G_1 + \Delta G_2 = 0$$

$$\text{or} \quad \Delta G_1 = \Delta G_2$$

$$\text{i.e.,} \quad V_1 \Delta P - S_1 \Delta T = V_2 \Delta P - S_2 \Delta T$$

$$\text{or} \quad \frac{\Delta P}{\Delta T} = \frac{S_2 - S_1}{(V_2 - V_1)} = \frac{\Delta S}{(V_2 - V_1)}$$

$$\text{i.e.,} \quad \frac{dP}{dT} = \frac{T \Delta S}{T(V_2 - V_1)} = \frac{L}{T(V_2 - V_1)}$$

where L is the latent heat of the process.

This is called the *Clapeyron Equation*. It may also be derived in other ways.

(b) From Maxwell's relations, (IV.68), we have

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

When two phases are in equilibrium, say a solid and a liquid or a liquid and a vapour, the vapour pressure is independent of the mass and hence, of the volume. Therefore, in such cases, we may write,

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\partial P}{\partial T}$$

Further, if we consider the latent heat of the change, L , as nearly constant and independent of temperature, we have

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \frac{\partial Q}{\partial V} = \frac{L}{T(V_2 - V_1)}$$

$$\text{Thus,} \quad \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad \dots (IV.82)$$

V_2 and V_1 being the final and initial volumes of the system. The equation is applicable to all phase-changes.

The sign of $\frac{dP}{dT}$ depends on the signs of L and ΔV . Thus, if L is positive and $V_2 > V_1$, there would be a rise in pressure with increase in temperature. In the evaporation of a liquid these conditions prevail, and as such, the vapour pressure increases with rise in temperature. In the melting of a solid, L is positive and if $V_l > V_s$, melting temperature would increase with pressure as in the case of paraffin. But if $V_l < V_s$, higher pressure will lower the melting temperature, as in the case of ice.

This relation would also apply to the transformation of one modification of a solid to another, say α -sulphur to β -sulphur; L would, of course, mean the heat of transformation.

The Clapeyron-equation (IV.82) may be simplified in the case of vaporisation of a substance. In such a case, the relation is,

$$\frac{\partial P}{\partial T} = \frac{L}{T(V_g - V_l)}, \quad \begin{array}{l} (V_g = \text{volume of gas,} \\ V_l = \text{volume of liquid).} \end{array}$$

Since $V_l \ll V_g$, so approximately,

$$\frac{\partial P}{\partial T} = \frac{L}{TV_g} = \frac{L}{T \cdot RT/P} = \frac{L \cdot P}{RT^2}, \quad (\text{for one mole})$$

assuming the vapour to behave as a perfect gas.

$$\therefore \frac{1}{P} \frac{dP}{dT} = \frac{L}{RT^2} \quad \dots (IV.83)$$

$$\text{or} \quad \frac{d \ln P}{dT} = \frac{L}{RT^2} \quad \dots (IV.84)$$

where L is the latent heat per gm.-mole.

If we further assume that the latent heat practically remains constant in the temperature range T_1 to T_2 , the integration of this relation gives,

$$\int_{P_2}^{P_1} d \ln P = \int_{T_2}^{T_1} \frac{L}{RT^2} dT$$

$$\text{or} \quad \ln \frac{P_1}{P_2} = -\frac{L}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots (IV.85)$$

$$\text{i.e.,} \quad \log \frac{P_1}{P_2} = -\frac{L}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots (IV.86)$$

It is needless to mention that this relation is also applicable to sublimation processes where L would be the latent heat of sublimation.

Problems : (i) Calculate the freezing temperature of water if the pressure be increased by one atmosphere. (Latent heat of fusion = 80 cal./gm.)

From equation (VIII.25), we have

$$\frac{\Delta P}{\Delta T} = \frac{L}{T(V_{\text{ice}} - V_{\text{water}})}$$

$$\therefore \Delta T = \frac{\Delta P \cdot T(V_{\text{ice}} - V_{\text{water}})}{L} = \frac{13.6 \times 981 \times 76 \times 273 \times .09}{-(80 \times 4.2 \times 10^7)} = -0.008^\circ\text{C}.$$

(ii) Calculate the specific volume of ether-vapour at its boiling point (35°C). Given

$L = 86 \text{ cal./gm.}$, $\frac{\partial P}{\partial T} = 27 \text{ mm.}$ and density of liquid ether = 0.7 gm./c.c.

$$\text{We know,} \quad \frac{\partial P}{\partial T} = \frac{L}{T(V_g - V_l)}$$

$$\text{or,} \quad 2.7 \times 13.6 \times 981 = \frac{86 \times 4.2 \times 10^7}{\left(273 + 35\right) \left(V_g - \frac{1}{0.7}\right)}$$

$$\text{whence,} \quad V_{\text{gas}} = 322 \text{ c.c.}$$

i.e., the specific volume of ether vapour = 322 c.c.

(iii) Under what pressure will water boil at 101°C ? ($L = 536 \text{ cal./gm.}$)

Using equation (VIII.26)

$$\Delta P = \frac{L \cdot P}{RT^2} \Delta T = \left[\frac{18 \times 536}{2 \times 373^2} \times 760 \times 1 \right] \text{ mm.} = 27 \text{ mm.}$$

Hence, water would boil at 101°C at 787 mm. pressure.

(iv) The densities of α - and β -sulphur are 2.00 and 1.95 respectively at their transition temperature, 96°C . The transition temperature changes by 0.036° for every atmosphere rise in pressure. Find out the heat of transition.

$$\frac{\Delta P}{\Delta T} = \frac{\Delta H}{T(V_\beta - V_\alpha)}$$

$$\text{or} \quad \Delta H = \frac{\Delta P}{\Delta T} \cdot T(V_\beta - V_\alpha) = \frac{1}{0.036} \times (273 + 96) \left[\frac{1}{1.95} - \frac{1}{2.00} \right] \text{ c.c.-atm.}$$

$$= 3.16 \text{ calories per gm.}$$

IV.46. Trouton's Rule. From equation (IV.84), we have, for the vaporisation of a liquid,

$$\ln P = -\frac{L}{RT} + C_1 \text{ (for 1 gm-mole)} \quad \dots \text{ (IV.87)}$$

If we consider the liquids at their boiling temperatures T_b , then the pressure P will be one atmosphere (i.e., $P = 1$).

$$\text{or} \quad \frac{L}{T_b} = R.C_1 = C \text{ (constant).}$$

where L is the molar latent heat of vaporisation.

Trouton had made this important generalisation from experimental observations and stated that *the ratio of the molar heat of vaporisation to the boiling temperature is a constant for simple or non-associated liquids and the constant is approximately 21*. In other words, the molar entropy-change on vaporisation at the boiling temperature is constant. In Table A below are given the entropy-changes for some liquids at their boiling-temperatures.

TABLE A : MOLAR ENTROPY-CHANGES OF VAPORISATION

Substance	B.Pt. ($^{\circ}\text{C}$)	$\frac{L}{T_b}$	Substance	B.Pt. ($^{\circ}\text{C}$)	$\frac{L}{T_b}$
<i>n</i> -Hexane	68.7	20.28	Hydrogen bromide	- 67	21.0
<i>n</i> -Heptane	98.4	20.61	Hydrogen fluoride	104	16.0
<i>n</i> -Octane	125.6	20.96	Oxygen	-183	18.0
Benzene	80.1	20.81	Nitrogen	-196	17.3
Toluene	110.6	20.85	Hydrogen	-257	15.61
<i>o</i> -Xylene	144.4	21.07	Water	100	28.7
<i>m</i> -Xylene	139.0	21.10	Ammonia	- 33	24.2
<i>p</i> -Xylene	138.4	20.95	Zinc	907	23.5
Carbon disulphide	46	21.0	Cadmium	767	22.9
Hydrogen chloride	-85	21.7	Mercury	357	22.4

It is observed that Trouton's Rule fails for liquids which are associated and also in the case of low-boiling or high-boiling liquids. Hildebrand modified Trouton's Rule and suggested that molar entropy-changes should be compared at temperatures when the vapours are in *equal concentrations* and not at unit atmosphere. Arbitrarily, the concentration chosen was 0.005 moles per litre, the entropy-change per mole, $\Delta S = \frac{L}{T_e}$, where T_e is the temperature having the aforesaid concentration. Table B gives the values obtained on this basis.

TABLE B : ENTROPY-CHANGES (HILDEBRAND'S RULE)

Substance	$\Delta S = \frac{L}{T_e}$	Substance	$\Delta S = \frac{L}{T_e}$
Oxygen	27.6	Zinc	26.4
Nitrogen	27.6	Cadmium	26.4
Hexane	27.2	Mercury	26.2
Benzene	27.4	Alcohol	32.0
Octane	27.6	Water	32.0
Carbon tetrachloride	27.0		

IV. VAPOUR-PRESSURE EQUATION : CHEMICAL CONSTANTS

IV.47. Vapour-Pressure Relation. The Clapeyron equation (IV.82) is used also in obtaining an expression for the vapour pressure of substances in the condensed state—solids or liquids—specially at very low temperatures. At low temperatures,

the vapour pressures are so small that the vapours may be regarded to behave as ideal gases. From Kirchhoff's equation, we have,

$$\Delta H_T - \Delta H_0 = \int_0^T \Delta C_P dT$$

In vaporisation the heat-changes are the latent heats. So,

$$L_T - L_0 = \int_0^T \Delta C_P dT$$

or the latent heat at any temperature T ,

$$L_T = L_0 + \int_0^T (C_{P_g} - C_{P_c}) dT \quad \dots (IV.88)$$

where C_{P_g} = heat-capacity of the vapour and C_{P_c} = heat-capacity in the condensed state (solid or liquid). Now, the Clapeyron equation is

$$\frac{\partial \ln P}{\partial T} = \frac{L_T}{RT^2}$$

Introducing (IV.88),

$$\frac{\partial \ln P}{\partial T} = \frac{L_0 + \int_0^T C_{P_g} dT - \int_0^T C_{P_c} dT}{RT^2}$$

Integrating,

$$\ln P = -\frac{L_0}{RT} + \int_0^T \frac{dT}{RT^2} \int_0^T C_{P_g} dT - \int_0^T \frac{dT}{RT^2} \int_0^T C_{P_c} dT + Z_1$$

(Z_1 is a constant) \dots (IV.89)

Now, if we assume ideal behaviour for the vapour and if the vapour be monatomic, (which is true in the case of metals especially), we have $C_{P_g} = (5/2) R$. Then,

$$\ln P = -\frac{L_0}{RT} + \frac{5}{2} \ln T - \int_0^T \frac{dT}{RT^2} \int_0^T C_{P_c} dT + Z_1$$

$$\begin{aligned} \text{or } \ln P &= -\frac{L_0}{RT} + \frac{5}{2} \ln T + \frac{1}{RT} \int_0^T C_{P_c} dT - \int_0^T \frac{C_{P_c}}{RT} dT + Z_1 \\ &= -\frac{L_0}{RT} + \frac{5}{2} \ln T + \frac{1}{RT} \int_0^T C_{P_c} dT - \frac{1}{R} \int_0^T C_{P_c} d \ln T + Z_1 \end{aligned}$$

\dots (IV.90)

Expressing the pressure in atmospheres and converting into Briggsian logarithms,

$$\begin{aligned} \log_{10} P &= -\frac{L_0}{2.303 RT} + \frac{5}{2} \log_{10} T + \frac{1}{2.303 RT} \int_0^T C_{P_c} dT - \\ &\quad \frac{1}{2.303 R} \int_0^T C_{P_c} d \ln T + \frac{Z_1}{2.303} - \log (1.014 \times 10^6). \end{aligned}$$

Putting $\frac{Z_1}{2.303} - \log (1.014 \times 10^6) = i$ (constant),

$$\log_{10} P = -\frac{L_0}{2.303 RT} + \frac{5}{2} \log_{10} T + \frac{1}{2.303 RT} \int_0^T C_{P_c} dT - \frac{1}{2.303 RT} \int_0^T C_{P_c} d \ln T + i \quad \dots \text{(IV.91)}$$

where i is called the *vapour-pressure constant* or the *chemical constant*. It shows that the knowledge of the chemical constant with some thermal data would enable us to calculate the vapour pressure of substances at very low temperatures. The chemical constant values of many substances have now been determined accurately.

This, of course, would require the knowledge of $\int_0^T C_{P_c} dT$ and $\int_0^T C_{P_c} d \ln T$.

Usually C_{P_c} is determined at different temperatures starting from the absolute zero (with necessary extrapolation) to the temperature as required. The C_{P_c} -values are plotted against T and the area under the curve up to T -axis gives the value of $\int_0^T C_{P_c} dT$. Similarly, plotting C_{P_c} against $\log_{10} T$, the values of $\int_0^T C_{P_c} d \ln T$ are also found out. Now, from equation (IV.91),

$$\begin{aligned} \log_{10} P - \frac{5}{2} \log T - \frac{1}{2.303 RT} \int_0^T C_{P_c} dT + \frac{1}{2.303 R} \int_0^T C_{P_c} d \ln T \\ = -\frac{L_0}{2.303 RT} + i \end{aligned}$$

Plotting the expression on the left-hand against $1/T$, a straight line is obtained, the intercept gives the value of i and the slope $= -L_0/2.303 R$. (Fig. IV.27)

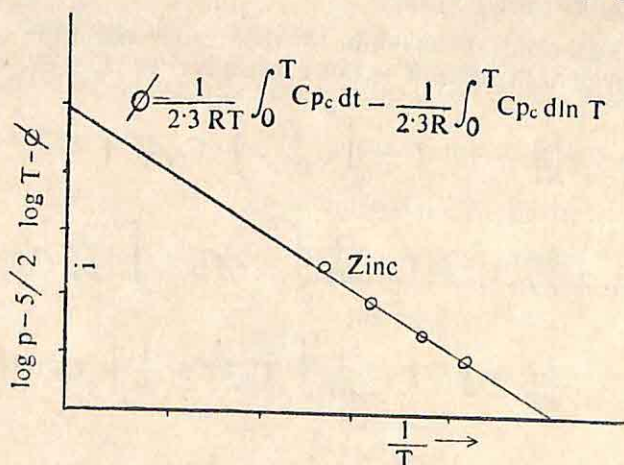


FIG. IV.27. Determination of vapour-pressure constant

When a high degree of accuracy is not required, some empirical relations are often used to calculate the vapour pressure in place of equation (IV.91), such as

$$(i) \ln P = A - \frac{B}{T} + C \ln T \text{ (Kirchhoff, Rankine, etc.)}$$

$$(ii) \log_{10} P = -\frac{L_0}{RT} + 1.75 \log_{10} T - \frac{b}{R} T + i'$$

IV.48. The Entropy and the Chemical Constant. It is also possible to obtain a relation between the vapour pressure constant and the entropy of a substance.

Suppose we start with a gm-mole of a pure solid substance at absolute zero and finally convert it into vapour at a temperature T under a standard pressure P_0 (usually one atmosphere). Let us calculate the entropy-change of the transformation.

Firstly, the solid is heated from 0° to $T^\circ\text{K}$, $\Delta S_1 = \int_0^T C_{P_c} d \ln T$

Secondly, the solid is vaporised at $T^\circ\text{K}$, $\Delta S_2 = \frac{L_T}{T}$

Finally, the vapour is changed from its own vapour pressure P to the standard pressure P_0 , $\Delta S_3 = R \ln \frac{P}{P_0}$

Hence, net entropy-change,

$$S_{T(\text{gas})} - S_{0(\text{cond})} = \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\text{i.e.,} \quad \Delta S = \int_0^T C_{P_c} d \ln T + \frac{L_T}{T} + R \ln \frac{P}{P_0}$$

$$\text{or} \quad R \ln \frac{P}{P_0} = -\frac{L_T}{T} - \int_0^T C_{P_c} d \ln T + \Delta S$$

$$= -\frac{L_0 + \int_0^T C_{P_g} dT - \int_0^T C_{P_c} dT}{T} - \int_0^T C_{P_c} d \ln T + \Delta S$$

$$\text{Since, } P_0 = 1, \quad \ln P = -\frac{L_0}{RT} - \frac{1}{RT} \int_0^T C_{P_g} dT + \frac{1}{RT} \int_0^T C_{P_c} dT$$

$$- \frac{1}{R} \int_0^T C_{P_c} d \ln T + \frac{S_T - S_0}{R}$$

$$= -\frac{L_0}{RT} - \frac{5}{2} + \frac{1}{RT} \int_0^T C_{P_c} dT - \frac{1}{R} \int_0^T C_{P_c} d \ln T + \frac{S_T - S_0}{R}$$

$$[\because C_{P_g} = \frac{5}{2} R]$$

$$\begin{aligned} \text{Hence, } \log_{10} P = & -\frac{L_0}{2.303 RT} - \frac{5}{2 \times 2.303} + \frac{1}{2.303 RT} \int_0^T C_{P_c} dT - \\ & \frac{1}{2.303 R} \int_0^T C_{P_c} d \ln T + \frac{S_T - S_0}{R \times 2.303} \quad \dots \text{ (IV.92)} \end{aligned}$$

Comparing equations (IV.91) and (IV.92), we have

$$\frac{-5}{2 \times 2.303} + \frac{S_T - S_0}{R \times 2.303} = \frac{5}{2} \log_{10} T + i$$

$$\text{or} \quad S_T = S_0 + \frac{5}{2} R + \frac{5}{2} R \times 2.303 \log_{10} T + 2.303 R \times i$$

Anticipating from the third Law of Thermodynamics, that $S_0 = 0$, i.e., entropy of a pure solid at 0°K is zero, we have

$$S_T = \frac{5}{2} R + \frac{5}{2} R \times 2.303 \log_{10} T + 2.303 R \times i \quad \dots \text{ (IV.93)}$$

The knowledge of chemical constant thus predicts the value of entropy of a pure monatomic vapour.

It can be shown from consideration of statistical thermodynamics that the vapour pressure constant i may be represented as, (Chap. VIII),

$$i = \log_{10} \left[\frac{g(2\pi mk)^{3/2} \cdot k}{1.013 \times 10^9 \times h^3} \right]$$

and

$$S_T = R \left[\ln \frac{g(2\pi mkT)^{3/2}}{h^3} \cdot \frac{kT}{P} + \frac{5}{2} \right]$$

The values of i determined from vapour-pressure formula and calculated as above show remarkable identity.

TABLE : VAPOUR PRESSURE CONSTANTS. (P in atm.)

Gas	i (calc)	i (obs.)	Gas	i (calc)	i (obs)	Gas	i (calc)	i (obs)
He	-0.68	-0.69	Zn	1.136	1.26	N ₂	-0.175	-0.19
Ar	0.81	0.83	Cu	1.11	1.40	O ₂	0.53	0.57
Na	0.757	0.78	Hg	1.87	1.99	Cl ₂	1.35	1.74
K	1.02	1.13	Cd	1.49	1.57	I ₂	2.99	3.10
Mg	0.49	0.49	Tl	2.18	2.40	HCl	-0.42	-0.43

NERNST HEAT THEOREM. THE THIRD LAW

We have so far discussed the first and the second Laws with their simple applications. We may now turn our attention to the other law of experience, the Third Law, which is of great importance in the study of chemical changes.

IV.49. Limitations of the Gibbs-Helmholtz Relation. The Gibbs Helmholtz equation,

$$\Delta G - \Delta H = T \left(\frac{\partial(\Delta G)}{\partial T} \right)_P$$

correlates the heat-change (ΔH) with the change in thermodynamic or Gibbs potential (ΔG) in a process.

Some special cases may arise, such as

(i) When $\frac{\partial(\Delta G)}{\partial T} = 0$, i.e., when temperature coefficient of the Gibbs potential change is nil, $\Delta G = \Delta H$. Examples may be found in some processes occurring in galvanic cells, say the Daniell cell.

(ii) When ΔG is almost zero, $\Delta H = -T \frac{\partial(\Delta G)}{\partial T}$. Such cases would be found in the fusion of solids at their melting points where ΔG becomes almost nil, but ΔH is appreciably large.

(iii) When $T = 0$, $\Delta G = \Delta H$. This equality of heat-change and Gibbs potential change is of theoretical importance but hardly of any practical importance as we cannot carry out a process at absolute zero.

Excepting in these cases, in all other transformations there is an inequality between ΔG and ΔH . It is obvious from the equation that a knowledge of ΔG would enable us to ascertain ΔH of a process. But the reverse is not true. We can often measure the heat-change, ΔH (calorimetrically or otherwise), but this thermal data does not permit us to ascertain the Gibbs potential change, ΔG . This is the limitation of the Gibbs-Helmholtz relation. For a long time it was a problem of considerable interest, particularly in the field of chemical changes, to develop a method of ascertaining ΔG from measurable thermal data. We owe to Nernst a successful solution to this problem.

IV.50. Nernst Heat Theorem. In 1902 Richards studied the thermodynamic changes in a number of galvanic cells at low temperatures and showed that with lowering

of temperature ΔG and ΔH approach each other rapidly. That is, at extremely low temperatures, ΔG and ΔH tend to become equal. Hence,

$$\text{Lt}_{T \rightarrow 0}, \Delta G = \Delta H$$

From Gibb's Helmholtz relation, we have, $\text{Lt}_{T \rightarrow 0}, T \frac{\partial(\Delta G)}{\partial T} = 0$

We already know that at absolute zero ($T = 0$), $T \frac{\partial(\Delta G)}{\partial T}$ will be equal to zero, whether $\frac{\partial(\Delta G)}{\partial T}$ is a finite quantity or zero. In 1906, Nernst made the bold postulate that for a process in a condensed system $\frac{\partial(\Delta G)}{\partial T}$ will be zero in the vicinity of absolute zero. That is,

$$\text{Lt}_{T \rightarrow 0} \frac{\partial(\Delta G)}{\partial T} = 0 \quad \dots (A)$$

The variation of ΔG with temperature might then be graphically represented as in Fig. (IV.28). It is to be remembered that with lowering of temperature the magnitude of ΔG may increase or decrease, but at extremely low temperatures, ΔG would be constant.

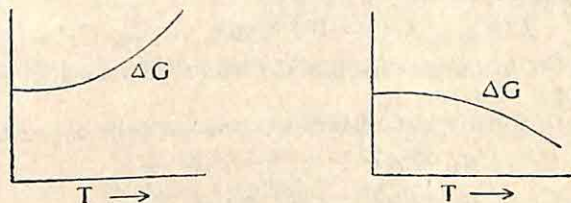


FIG. IV.28

Nernst further suggested that not only ΔG and ΔH are equal at the absolute zero, but they approach equality in this temperature range asymptotically. The equality holds true for some range above and in the neighbourhood of absolute zero. Hence, the variation of ΔG and ΔH may be represented graphically as in Fig. (IV.29).

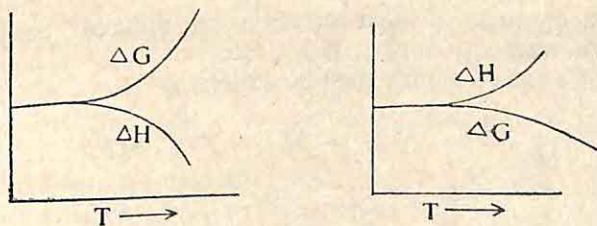


FIG. IV.29

It leads to the conclusion that, $\text{Lt}_{T \rightarrow 0}, \frac{\partial(\Delta H)}{\partial T} = 0 \quad \dots (B)$

It is easy to see that if ΔG increases with temperature in a process, ΔH will diminish and *vice versa*.

$$\begin{aligned} \text{For,} \quad & \Delta G - \Delta H = T \frac{\partial(\Delta G)}{\partial T} \\ \text{i.e.,} \quad & \frac{\partial(\Delta G)}{\partial T} - \frac{\partial(\Delta H)}{\partial T} = T \frac{\partial^2(\Delta G)}{\partial T^2} + \frac{\partial(\Delta G)}{\partial T} \\ \text{or} \quad & -\frac{\partial(\Delta H)}{\partial T} = T \frac{\partial^2(\Delta G)}{\partial T^2}. \end{aligned}$$

The two terms $\frac{\partial(\Delta H)}{\partial T}$ and $\frac{\partial^2(\Delta G)}{\partial T^2}$ are opposite in sign.

Since by Nernst postulate ΔG converges to a limiting value at low temperatures, so both the terms $\frac{\partial(\Delta G)}{\partial T}$ and $\frac{\partial^2(\Delta G)}{\partial T^2}$ must have the same sign. Hence, $\frac{\partial(\Delta H)}{\partial T}$ and $\frac{\partial(\Delta G)}{\partial T}$ must have opposite signs. That is, ΔG would increase with temperature if ΔH diminishes and vice versa.

Stated analytically, the two postulates of Nernst for a condensed system are

$$\left. \begin{aligned} \lim_{T \rightarrow 0} \frac{\partial(\Delta G)}{\partial T} &= 0 \\ \lim_{T \rightarrow 0} \frac{\partial(\Delta H)}{\partial T} &= 0 \end{aligned} \right\} \dots \text{(IV.94)}$$

These constitute what we call Nernst Heat Theorem. This innocent-looking pair of simple relations have however far-reaching consequences as we shall presently see.

(i) Now, from Kirchhoff's equation, (at constant pressure)

$$\frac{\partial(\Delta H)}{\partial T} = \Delta C_P = C_f - C_i$$

where C_f and C_i are the heat-capacities of the system at the final and initial states.

Then, from equation (IV.94), we find,

$$\lim_{T \rightarrow 0} \Delta C_P = 0; \text{ hence, } \lim_{T \rightarrow 0} C_f = C_i$$

It means that the *heat-capacity would remain unchanged in any transformation in the vicinity of absolute zero.*

Again, the heat-capacity at constant pressure may be expressed as

$$C_f = a_2 + b_2T + c_2T^2 + d_2T^3 + \dots$$

$$C_i = a_1 + b_1T + c_1T^2 + d_1T^3 + \dots$$

$$\text{or } \Delta C_P = a + \beta T + \gamma T^2 + \delta T^3 + \dots$$

It is assumed that these relations are valid at low temperatures (which is not strictly correct). When $T = 0$, $\Delta C_P = 0$; therefore,

$$\Delta C_P = 0 = a + 0 + 0 + \dots$$

$$\text{or } a = 0$$

$$\text{Hence, } \Delta C_P = \beta T + \gamma T^2 + \delta T^3 + \dots \dots \text{(IV.95)}$$

Thermal measurement of heat-capacities at different temperatures would enable us to find the values of constants β , γ , etc.

The Kirchhoff's equation may then be written as

$$\frac{\partial(\Delta H)}{\partial T} = \Delta C_P = \beta T + \gamma T^2 + \delta T^3 + \dots$$

$$\text{or, } \Delta H_T - \Delta H_0 = \int_0^T (\beta T + \gamma T^2 + \delta T^3 + \dots) dT$$

where ΔH_0 is the heat-change at absolute zero.

$$\text{So, } \Delta H_T = \Delta H_0 + \frac{\beta}{2} T^2 + \frac{\gamma}{3} T^3 + \frac{\delta}{4} T^4 + \dots \dots \text{(IV.96)}$$

The knowledge of ΔH_T at a given temperature, with the aid of equation (IV.95), gives the magnitude of ΔH_0 .

(ii) Again, we know from definition,

$$\Delta G = VdP - SdT$$

$$\text{or } \frac{\partial(\Delta G)}{\partial T} = -\Delta S, \text{ (at constant pressure)} \dots \text{(IV.97)}$$

But in the vicinity of absolute zero, $\frac{\partial(\Delta G)}{\partial T} = 0$,

Hence, $\lim_{T \rightarrow 0} \Delta S = 0$; i.e., $S_2 - S_1 = 0$
 $\therefore S_2 = S_1$

In other words, in the neighbourhood of absolute zero, all processes should occur without alteration in entropy-values.

(iii) Since $\frac{\partial(\Delta H)}{\partial T} = \Delta C_P$, then $\frac{\partial(\Delta S)}{\partial T} = \frac{\Delta C_P}{T}$

or, $\Delta S = \int \frac{\Delta C_P}{T} dT + Z$ (constant)

When $\lim_{T \rightarrow 0} \Delta S = 0$ and also $\Delta C_P = 0$. Further, $\frac{\Delta C_P}{T}$ is finite or zero. Hence, $Z = 0$.

So,
$$\Delta S = \int \frac{\Delta C_P}{T} dT \quad \dots (IV.98)$$

Substituting equation (IV.95), we can write,

$$\Delta S = \int \left(\frac{\beta T + \gamma T^2 + \delta T^3 + \dots}{T} \right) dT = \beta T + \frac{\gamma}{2} T^2 + \frac{\delta}{3} T^3 + \dots$$

The Gibbs-Helmholtz relation then may be expressed as,

$$\begin{aligned} \Delta G_T &= \Delta H_T + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_P \\ \Delta G_T &= \Delta H_T - T \Delta S \\ \Delta G_T &= \Delta H_T - T \int \frac{\Delta C_P}{T} dT \quad \dots (IV.99) \end{aligned}$$

Substituting the value of ΔS ,

$$\begin{aligned} \Delta G_T &= \Delta H_T - T \left[\beta T + \frac{\gamma}{2} T^2 + \frac{\delta}{3} T^3 + \dots \right] \\ &= \left[\Delta H_0 + \frac{\beta}{2} T^2 + \frac{\gamma}{3} T^3 + \frac{\delta}{4} T^4 + \dots \right] - \left[\beta T^2 + \frac{\gamma}{2} T^3 + \frac{\delta}{3} T^4 + \dots \right] \\ \text{or } \Delta G_T &= \Delta H_0 - \frac{\beta}{2} T^2 - \frac{\gamma}{6} T^3 - \frac{\delta}{12} T^4 - \dots (IV.100) \end{aligned}$$

The problem of determining the Gibbs potential change, ΔG , from thermal data for systems involving solids is thus solved with the help of this equation, derived from the Nernst Heat theorem.

IV.51. Applications of Nernst Heat Theorem. The usefulness and validity of the theorem may be illustrated by some historically well-known examples.

(a) *Transition point of sulphur*: In the transformation of α and β -sulphur, we may write, from equation (IV.95),

$$\Delta C_P = \beta T$$

Measuring the heat-capacities of the two forms at a known temperature, the value of β was found to be 2.30×10^{-5} . The heat of transformation ΔH_T at a temperature T was also measured, from which ΔH_0 was calculated as 1.57; for

$$\Delta H_0 = \Delta H_T - \frac{\beta}{2} T^2 = 1.57$$

At the transition temperature T_c , the two modifications of sulphur are in equilibrium, i.e., $\Delta G_{T_c} = 0$.

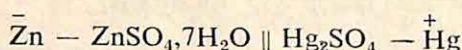
$$\text{Hence } \Delta H_0 - \frac{\beta}{2} T_c^2 = 1.57 - 1.15 \times 10^{-5} T_c^2 = 0$$

$$\text{or } T_c = 369.5^\circ \text{K.}$$

The experimentally observed value, $T_c = 368.4^\circ \text{K.}$

The fusion temperature of solids may also be similarly calculated.

(b) *The e.m.f. of a voltaic cell.* With the help of Nernst Heat Theorem, the e.m.f. can be calculated from the thermal data. Let us take the cell,



The changes involved are,

	heat-change
$\text{Zn} \rightarrow \text{Zn}^{++}$	Q_1
$\text{Zn}^{++} \rightarrow \text{ZnSO}_4$	Q_2
$\text{ZnSO}_4 + 7\text{H}_2\text{O} \rightarrow \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	Q_3
$\text{Hg}_2^{++} \rightarrow \text{Hg}_2$	Q_4

The net heat-change at 10°C , $\Delta H_T = \Sigma Q = -33360$ cals per gm-equivalent from calorimetric measurements.

The heat-capacities of the initial and final components were also measured at the same temperature to obtain $\Delta C_{P_{283}} = 0.95$, whence $\beta = 0.0034$.

$$\text{Then } \Delta H_0 = \Delta H_T - \frac{\beta}{2} T^2 = -33360 - 0.0017 \times 283^2 = -33505 \text{ cal.}$$

$$\text{So, } \Delta G = \Delta H_0 - \frac{\beta}{2} T^2$$

The Gibbs potential change is the net electric energy obtained.

$$\therefore \Delta G = -nFE = -33505 - 0.0017 \times 283^2$$

$$\text{whence } E = 1.459 \text{ volts.}$$

$$\text{The experimental value is } E = 1.462 \text{ volts.}$$

We shall see later that the most useful application of the Heat Theorem is in the calculation of equilibrium constants of chemical changes.

IV.52. The Third Law of Thermodynamics. Even though there are limitations, the Nernst Heat Theorem is the precursor of the more important fundamental principle enunciated by Planck commonly called the Third Law. One of the consequences of the Heat Theorem is

$$\text{Lt}_{T \rightarrow 0}, \Delta C_P = 0$$

i.e., heat-capacities of all substances (reactants or resultants) at absolute zero must be the same.

From quantal principles, it was found that at very low temperatures, the heat-capacity C_P of a substance continuously diminishes with lowering of temperature and would ultimately vanish ;

$$\text{i.e., } \text{Lt}_{T \rightarrow 0}, C_P = 0$$

This is also corroborated by experiments. Hence at low temperature $\frac{C_P}{T}$ is zero or a finite quantity. The entropy change due to lowering of temperature is given by

$$\Delta S = \frac{\Delta q}{T} = \frac{C_P dT}{T}$$

$$\text{or} \quad \int_0^T dS = \int_0^T \frac{C_P dT}{T}$$

$$\text{i.e.,} \quad S_T - S_0 = \int_0^T \frac{C_P}{T} dT$$

Since $\frac{C_P}{T}$ is a finite quantity, we can say $S_T - S_0$ must be a positive quantity i.e., $S_T > S_0$. In other words, the entropy of a substance at any temperature must be greater than its entropy at absolute zero.

In 1912 Planck made the striking proposal in this regard and enunciated the third law as

"The entropy of a solid or a liquid is zero at the absolute zero of temperature."

For a condensed system,

$$\begin{aligned} \text{(i) Nernst theorem states} \quad & \text{Lt}_{T \rightarrow 0}, \quad \Delta S = 0 \\ \text{and (ii) Planck's Law states} \quad & \text{Lt}_{T \rightarrow 0}, \quad S = 0 \end{aligned}$$

It is obvious that the third law does not contradict the Heat Theorem rather it supports and makes the later quantitative. At 0°K , the reactant solids have zero entropy as also the products have zero entropy, hence the entropy-change, $\Delta S = 0$.

It was shown in Sec. IV.36, the entropy can be expressed from statistical considerations as

$$S = k \ln W.$$

where W is the probability of distribution. At absolute zero, if the substance be in a crystalline state, when all the constituent atoms are in the lowest energy levels, there is only one possible state or W is unity. Hence,

$$\text{Lt}_{T \rightarrow 0}, S = k \ln 1 = 0.$$

In the case of a supercooled liquid or in the case of mixtures or solutions, the thermodynamic probability may not be unity, and as such even at absolute zero, S will not be zero. Thus, the principle enunciated by Planck would be true in case of *pure crystalline substances*. The Third Law, therefore, has been stated as,

"Every system has a finite positive entropy but at the absolute zero of temperature the entropy may become zero and does so become in the case of a pure crystalline substance" (Lewis and Randall).

IV.53. Consequences of the Third Law. From the third law we can arrive at a number of generalisations, all of which are not derivable from the Heat Theorem.

(i) The entropy-change of a system due only to a small pressure-change, for a process near 0°K may be expressed, as

$$\Delta S = \int \left(\frac{\partial S}{\partial P} \right)_T dP$$

$$\text{But at } 0^\circ\text{K}, \Delta S = 0, \text{ hence } \left(\frac{\partial S}{\partial P} \right)_T = 0$$

$$\text{By Maxwell's relations, } \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

$$\text{Hence, } \text{Lt}_{T \rightarrow 0}, \left(\frac{\partial V}{\partial T} \right)_P = 0.$$

$$\text{(ii) Similarly, for a small volume-change of the system, } \Delta S = \int \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$\text{and therefore at } 0^\circ\text{K}, \left(\frac{\partial S}{\partial V} \right)_T = 0.$$

By Maxwell's relations, $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

Hence, $\lim_{T \rightarrow 0} \left(\frac{\partial P}{\partial T}\right)_V = 0$

That is, at absolute zero both the pressure and volume coefficients are zero.

(iii) At a constant pressure, $\Delta S = \frac{\Delta q}{T} = \frac{C_P dT}{T}$

Integrating, $S = \int_0^T \frac{C_P dT}{T} + S_0$

where S_0 is a constant.

Now the Third law states that the value of S must be finite at all temperatures. This means that at absolute zero (when $T = 0$), C_P must be zero. Otherwise if at 0°K , C is finite, then S cannot be finite. Hence,

$$\lim_{T \rightarrow 0} C_P = 0$$

Similarly, at constant volume it can be shown, $\lim_{T \rightarrow 0} C_V = 0$

IV.54. Experimental Determination of Entropy. The most important application of the Third Law is in the measurement of the entropy of a substance. We have

$$S_T - S_0 = \int_0^T \frac{C_P}{T} dT$$

From the Third Law, for a pure crystalline substance, $S_0 = 0$. Hence,

$$S_T = \int_0^T \frac{C_P}{T} dT = \int_0^T C_P d \ln T = 2.303 \int_0^T C_P d \log T$$

This shows that if C_P be plotted against $\log T$ as in Fig. IV.30(I) or alternatively, $\frac{C_P}{T}$ plotted against T as in Fig. IV.30(II), the entropy S_T can be graphically computed from the shaded areas of the figures. Obviously it requires the knowledge of the heat capacities C_P from the temperature T to the absolute zero. In practice

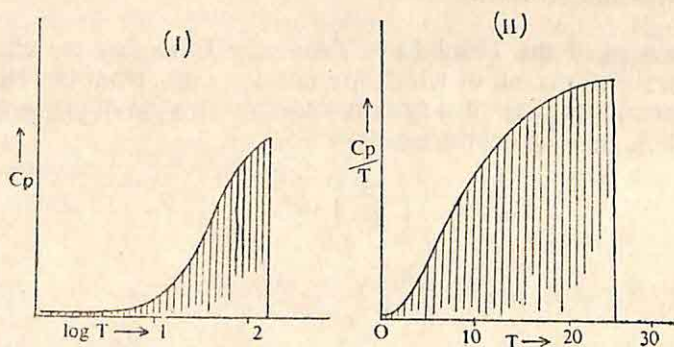


FIG. IV.30 The graphical determination of entropy

however C_P cannot be measured at absolute zero or near about it. The measurements of the heat-capacities are carried out to as low a temperature as that of liquid hydrogen. Below liquid hydrogen temperature, extrapolation is permissible with the aid of the Debye equation,

$$C_V = 464.5 \frac{T^3}{\theta^3}$$

where θ is a constant for the substance. From a determination of C_V at an appreciably higher temperature T , the magnitude of θ is known. Substituting θ in the

equation above, the values of C_V in the vicinity of absolute zero are calculated. At extremely low temperatures the differences of C_P and C_V are negligible, so that these values may be used for C_P in the extrapolation of the curves (Fig. IV.30).

Example : In the case of rhombic sulphur, the C_P values were calculated by Debye equation and $\frac{C_P}{T}$ vs. T was plotted.

The value of the entropy from 0°K to 30° K (Debye) = 0.12 cal/degree/mole.

The value of the entropy from 30°K to 298° K = 7.50 cal/degree/mole.

Hence, the net entropy of the rhombic sulphur per mole, (measured graphically), $S = 7.62$ cal/degree.

This method is also extended to determine the entropy of gases or liquids, in which the entropy-rise in the fusion or vaporisation of the substance are also to be added. In cases where the transi-

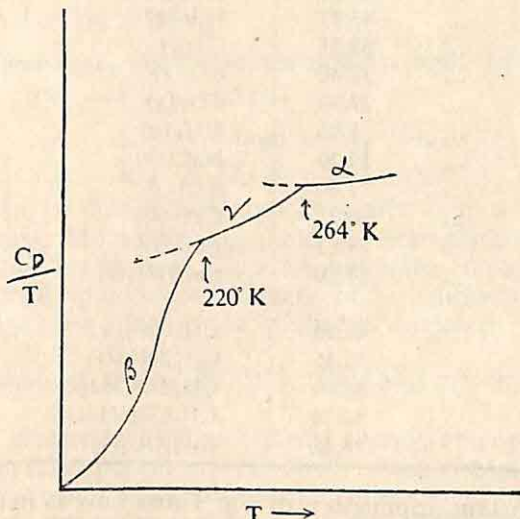


FIG. IV.31 The entropy of a mol of $\text{CH}_3\text{NH}_3\text{Cl}$ at 25°C

tion of solids occurs, the entropy-change due to transition must also be considered. Two examples are given below to illustrate the same.

Example 1. The entropy of methyl ammonium chloride (solid) at 25°C. (Aston et al, 1946).

The C_P -values were determined down to 12°K and in the region between 0°K and 12°K the values were calculated (Debye). Between 0°K and 298°K (25°C), there exist three different forms of solid, $\beta \rightarrow \gamma \rightarrow \alpha$ forms. The entropy-changes at the two transition temperatures at 220°K and 264°K were also considered from the heats of transition, (Fig. IV.31).

	ΔS
0°K—12°K (extrapolation)	0.067
12°K—220°K (β -form, graphically)	22.326
Transition ($\beta \rightarrow \gamma$) at 220°K	1.929 ($L = 425.2$)
220°K—264°K (γ -form, graphically)	3.690
Transition ($\gamma \rightarrow \alpha$) at 264°K	2.547 ($L = 673.6$)
264°K—298°K (α -form, graphically)	2.555
	33.114

$\therefore$ Entropy of one mole of solid $\text{CH}_3\text{NH}_3\text{Cl}$ at 298°K is 33.114 cal/degree.

Example 2. The entropy of ethylene gas at 25°C.

	ΔS
(i) 0°K—15°K (by extrapolation with Debye)	0.24
(ii) 15°K—104°K (graphically, $\frac{C_P}{T}$ vs T)	12.25
(iii) Fusion at 104°K ($L/T = 801/104$)	7.70
(iv) 104°K—169.4°K (graphically)	7.90
(v) Vaporisation at 169°K ($L/T = 3237/169.4$)	19.10
(vi) 169.4°K—298°K (graphically)	5.12

The entropy of a mole of ethylene at 25°C = 52.31 cal/degree

The entropy of gases thus determined corresponds to the real gases. For comparison, it is customary to express the gas-entropies in terms of ideal gases at one atm. usually at 25°C, introducing some corrections. This is called the *standard entropy* or the *absolute entropy* of a gas.

The absolute entropies of certain substances at 1 atm. and 25°C calculated from the thermal data are given below.

TABLE : THE ENTROPIES AT 298°K

Substance	Entropy	Substance	Entropy
H ₂ (g)	31.21	H ₂ O (l)	16.71
O ₂ (g)	49.00	HCl (g)	44.62
N ₂ (g)	45.77	HBr (g)	47.44
Cl ₂ (g)	53.31	HI (g)	49.31
Br ₂ (l)	36.40	CO (g)	47.30
I ₂ (s)	27.90	CO ₂ (g)	51.06
C (graphite)	1.36	NH ₃ (g)	46.80
Na (s)	12.20	NaCl (s)	17.30
S (rhombic)	7.60	KCl (s)	19.90
Fe (s)	6.71	CuO (s)	10.40
Zn (s)	9.83	BaO (s)	16.80
Hg (l)	17.80	Ca(OH) ₂ (s)	17.40
CH ₄ (g)	44.50	CH ₃ OH (l)	31.00
C ₂ H ₄ (g)	52.45	C ₂ H ₅ OH (l)	38.40
C ₂ H ₂ (g)	48.00	CH ₃ COCH ₃ (l)	47.80
C ₆ H ₆ (g)	64.34	CH ₃ COOH (l)	38.20
C ₆ H ₅ CH ₃ (g)	76.42	C ₂ H ₅ OC ₂ H ₅ (l)	60.40

The other important application of the Third Law is in the determination of equilibrium constants in chemical processes (See Chap. IX).

IV.55. Tests of the Third Law. Several experimental facts can be cited to establish the truth of the Third Law.

(a) It is a prediction of the Law that in the neighbourhood of the absolute zero, the heat-capacity and the coefficient of expansion would vanish. These have been confirmed experimentally in many instances.

(b) It is possible to calculate the change in entropy in the transition of one form of a substance into another form. The calculated values corroborate to the experimental result.

Suppose there are two crystalline forms *X* and *Y* of an element. At the transition temperature *T_t*, $\Delta G = 0$. Hence, the entropy change,

$$S_Y - S_X = \frac{\Delta H}{T} \quad \dots (a)$$

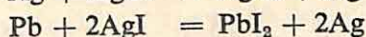
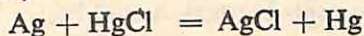
By the third Law, for both *X* and *Y*, the entropy value at *T* = 0 is zero, i.e., $S_X = S_Y = 0$ ($\lim_{T \rightarrow 0}$). Then at temperature *T_t*,

$$S_X = \int_0^{T_t} \frac{C_X}{T} dT \quad \text{and} \quad S_Y = \int_0^{T_t} \frac{C_Y}{T} dT$$

$$\text{or} \quad S_Y - S_X = \int_0^{T_t} \frac{C_Y - C_X}{T} dT \quad \dots (b)$$

The two methods (a) and (b) give the same value for the entropy-change. This has been studied in the case of white tin-gray tin, quartz-cristobalite, calcite-aragonite etc. The most satisfactory results were obtained with tin, which confirms the Third Law.

(c) In the reactions,

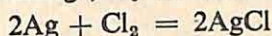


ΔG and ΔH were separately determined from (*e.m.f.*) and (calorimetric measurements) and ΔS is calculated. These values compared favourably with those obtained from the Third Law.

TABLE : ENTROPY-CHANGES

Chemical Process.	ΔS (Gibbs-Helmholtz)	ΔS (Third Law)
Sn (white)—Sn (grey)	- 1.87	- 1.94
$\text{Ag} + \text{HgCl} = \text{AgCl} + \text{Hg}$	+ 7.78	+ 7.70
$\frac{1}{2}\text{Pb} + \text{AgI} = \text{Ag} + \frac{1}{2}\text{PbI}_2$	- 3.99	- 3.69

(d) The entropy-change, say at room temperature, of the reaction



is given by

$$\Delta S = 2S_{\text{AgCl}} - 2S_{\text{Ag}} - S_{\text{Cl}_2}$$

or

$$S_{\text{Cl}_2} = 2S_{\text{AgCl}} - 2S_{\text{Ag}} - \Delta S$$

The value of ΔS can be determined experimentally from a knowledge of ΔG and ΔH of the process. Moreover, S_{AgCl} and S_{Ag} are ascertained from the heat-capacity data with the Third Law. Thus we know the entropy of chlorine, S_{Cl_2} . The value thus obtained approaches the value of S_{Cl_2} directly determined by the Third Law. This indeed is a proof of the validity of the Law.

PARTIAL MOLAL QUANTITIES : CHEMICAL POTENTIAL

The thermodynamic properties such as internal energy, entropy, free energy, etc., depend usually on the three parameters (P, V, T) of the system and can be defined by those parameters. The three parameters are interrelated by some equation of state, so that any two of them can be taken as independent variables. Thus, if X denotes any thermodynamic property of the system ; we can write

$$X = f(P, T), \quad X = f_1(V, T), \text{ etc.}$$

But this is true only for *closed* systems, *i.e.*, systems in which the mass and the chemical composition remain fixed. Now, in *open* systems in which the mass and the chemical composition may alter the thermodynamic functions, which are extensive properties like internal energy, enthalpy, entropy, free energy, Gibbs potential, volume, heat-capacity etc., must depend upon the amounts of the components present in the system.

So any extensive thermodynamic property, X , may be represented as,

$$X = f(P, T, n_1, n_2, n_3, n_4 \dots)$$

where $n_1, n_2, n_3 \dots$ etc. are the quantities of the different components in the system usually expressed in gm-moles.

IV.56. Partial Molal Quantities. Let us now consider small changes in all the variables of the system, including the amounts of the components. The net change in the thermodynamic property, X will be given by,

$$\begin{aligned} dX = & \left(\frac{\partial X}{\partial P} \right)_{T, n_1, n_2, \dots} dP + \left(\frac{\partial X}{\partial T} \right)_{P, n_1, n_2, \dots} dT + \left(\frac{\partial X}{\partial n_1} \right)_{P, T, n_2, n_3, \dots} dn_1 \\ & + \left(\frac{\partial X}{\partial n_2} \right)_{P, T, n_1, n_3, \dots} dn_2 + \left(\frac{\partial X}{\partial n_3} \right)_{P, T, n_1, n_2, \dots} dn_3 + \dots \end{aligned}$$

The term $\left(\frac{\partial X}{\partial n_1} \right)_{P, T, n_2, n_3, \dots}$ is called the *partial molal property* for the first component

and obviously denotes the rate of change of X on addition of one mole of the first component when all the other variables remain unchanged. This is usually denoted

by putting a bar over the symbol for the property, such as $\bar{X}_1$. The partial molal properties of the different components, then, would be,

$$\bar{X}_1 = \left(\frac{\partial X}{\partial n_1} \right)_{P,T,n_2,n_3,\dots}; \quad \bar{X}_2 = \left(\frac{\partial X}{\partial n_2} \right)_{P,T,n_1,n_3,\dots}; \quad \bar{X}_i = \left(\frac{\partial X}{\partial n_i} \right)_{P,T,n_1,n_2,\dots}$$

If the system undergoes a change only in the masses of its components, at *constant pressure and temperature*, then,

$$\begin{aligned} dX_{P,T} &= \left(\frac{\partial X}{\partial n_1} \right)_{P,T,n_2,n_3,\dots} dn_1 + \left(\frac{\partial X}{\partial n_2} \right)_{P,T,n_1,n_3,\dots} dn_2 + \dots + \left(\frac{\partial X}{\partial n_i} \right)_{P,T,n_1,n_2,\dots} dn_i + \dots \\ &= \bar{X}_1 dn_1 + \bar{X}_2 dn_2 + \dots + \bar{X}_i dn_i + \dots \end{aligned} \quad \dots \text{ (IV.101)}$$

It may be remembered that X stands for any extensive thermodynamic property. Thus, at constant temperature and pressure, we may express the changes of entropy as follows :

$$\begin{aligned} dS_{P,T} &= \left(\frac{\partial S}{\partial n_1} \right)_{P,T,n_2,n_3,\dots} dn_1 + \left(\frac{\partial S}{\partial n_2} \right)_{P,T,n_1,n_3,\dots} dn_2 + \dots + \left(\frac{\partial S}{\partial n_i} \right)_{P,T,n_1,n_2,\dots} dn_i + \dots \\ &= \bar{S}_1 dn_1 + \bar{S}_2 dn_2 + \dots + \bar{S}_i dn_i + \dots \end{aligned}$$

such that, partial molal entropy of the i th component $= \left(\frac{\partial S}{\partial n_i} \right)_{P,T,n_1,n_2,\dots} = \bar{S}_i$

Similarly, for the i th component in a system,

$$\text{Partial molal internal energy} = \left(\frac{\partial U}{\partial n_i} \right)_{P,T,n_1,n_2,\dots} = \bar{U}_i$$

$$\text{Partial molal enthalpy} = \left(\frac{\partial H}{\partial n_i} \right)_{P,T,n_1,n_2,\dots} = \bar{H}_i$$

etc. etc. etc.

IV.57. Chemical Potential. Consider a system containing n_1 moles of A_1 , n_2 moles of A_2 , ... n_i moles of A_i at pressure P and temperature T . Then its thermodynamic potential

$$G = f(P, T, n_1, n_2, \dots, n_i, \dots)$$

Suppose now the amounts of the constituents change at *constant pressure and temperature*.

The change in the Gibbs potential, G , may be expressed, at a constant temperature and pressure, in the same way as in eqn. (IV.101),

$$\begin{aligned} (dG)_{P,T} &= \left(\frac{\partial G}{\partial n_1} \right)_{P,T,n_2,n_3,\dots} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{P,T,n_1,n_3,\dots} dn_2 + \left(\frac{\partial G}{\partial n_3} \right)_{P,T,n_1,n_2,\dots} dn_3 + \dots \\ &= \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \bar{G}_3 dn_3 + \dots + \bar{G}_i dn_i + \dots \end{aligned} \quad \dots \text{ (IV.102)}$$

The partial molal Gibbs potential, [denoted by $\left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_1,n_2,\dots}$ for the i th component] has been given the name *chemical potential* by Willard Gibbs. It is universally represented by the symbol μ .

$$\text{That is,} \quad \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_1,n_2,\dots} = \bar{G}_i = \mu_i$$

$$\therefore dG_{P,T} = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots + \mu_i dn_i + \dots \quad \dots \text{ (IV.103)}$$

The chemical potential μ_i , therefore is a measure of the Gibbs potential increase of the system due to addition of 1 mole of the i th component at *constant temperature and pressure*, when other components remain unaltered. This, it would be soon realised, has a unique importance in dealing with the chemical processes,

Next imagine that at constant P and T , all the constituents are increased in the same proportion (Δx). That is, A_1 is increased by an amount $n_1 \Delta x$ moles, A_2 is increased by $n_2 \Delta x$ moles, ... A_i is increased by $n_i \Delta x$ moles. Hence,

$$dn_1 = n_1 \Delta x, dn_2 = n_2 \Delta x, dn_i = n_i \Delta x, \text{ etc.}$$

Since G is an extensive property, this will also increase by an amount $G \cdot \Delta x$, i.e.,

$$dG = G \cdot \Delta x.$$

Now, applying equation (IV.103), we can write

$$dG = \mu_1 n_1 \Delta x + \mu_2 n_2 \Delta x + \dots + \mu_i n_i \Delta x + \dots$$

$$\text{or } G \cdot \Delta x = \mu_1 n_1 \Delta x + \mu_2 n_2 \Delta x + \dots + \mu_i n_i \Delta x + \dots$$

$$\text{Hence, } G = \mu_1 n_1 + \mu_2 n_2 + \dots + \mu_i n_i + \dots = \sum \mu_i n_i.$$

Now complete differentiation of this equation gives us,

$$dG = (\mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots) + (n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \dots) \quad \dots \text{ (IV.104)}$$

Subtracting equation (IV.103) from equation (IV.104)

$$n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \dots = 0$$

We have thus three useful relations for chemical potentials with the composition of the system.

$$\left. \begin{aligned} \text{(i)} \quad G &= \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \dots = \sum \mu n \\ \text{(ii)} \quad dG &= \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \dots = \sum \mu dn \\ \text{(iii)} \quad 0 &= n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \dots = \sum n d\mu \end{aligned} \right\} \quad \dots \text{ (IV.105)}$$

These are commonly known as *Gibbs-Duhem relations*.

It must however be noted that the partial molal Gibbs potential (i.e., chemical potential) is independent of the masses but is not independent of the composition of the system. Though it means the increase of G of the system per mole of the added substance, but the increase depends upon the composition of the system. Thus if we add 1 gm-mole of water to (a) one kg of pure water and to (b) one kg of a salt solution, the increase in Gibbs potential will not be the same. To be more precise, it is the increase in the value of G at constant temperature and pressure from the addition of 1 mole of the component to an infinitely large quantity of the system such that the addition does not materially alter its composition. This also applies to other partial molal quantities, like partial molal volume, or partial entropy, etc. An attempt may now be made to express the chemical potential in terms of the parameters. We know,

$$\mu_i = \frac{dG}{dn_i}$$

$$\text{Hence, } \left[\frac{\partial \mu_i}{\partial P} \right]_T = \frac{d^2 G}{dn_i dP}$$

$$\text{Again, we have, } dG = VdP - SdT \quad \text{or} \quad V = \left[\frac{\partial G}{\partial P} \right]_T$$

$$\text{Therefore, } \left[\frac{\partial V}{\partial n_i} \right]_T = \frac{d^2 G}{dP dn_i}$$

$$\text{We have thus } \left[\frac{\partial \mu_i}{\partial P} \right]_T = \left[\frac{\partial V}{\partial n_i} \right]_T = \bar{V}_i \quad \dots \text{ (IV.106)}$$

The rate of change of chemical potential of a component of the system with pressure is equal to the partial molal volume of the component.

Now, suppose there is a system containing n gm-moles of a mixture of *ideal* gases at constant temperature T . Then, we know,

$$\text{(i)} \quad n = n_1 + n_2 + n_3 + n_4 + \dots + n_i + \dots$$

$$\text{(ii)} \quad V = (n_1 + n_2 + n_3 + \dots + n_i + \dots) \frac{RT}{P}$$

$$\text{(iii)} \quad P = p_1 + p_2 + p_3 + \dots + p_i + \dots$$

Consider a small change dn_i of the i th component, other variables remaining constant, then,

$$\bar{V}_i = \left[\frac{\partial V}{\partial n_i} \right]_{P, T, n_1, \dots} = \frac{RT}{P}$$

Again $p_i = n_i P$, or $\ln p_i = \ln n_i + \ln P$

$\therefore d \ln P = d \ln p_i$ (for a system of given composition)

Thus, from equation (IV.106),

$$d\mu_i = \bar{V}_i dP = \frac{dV}{dn_i} dP = \frac{RT}{P} dP.$$

or

$$d\mu_i = RT d \ln P = RT d \ln p_i$$

$\therefore$

$$\mu_i = RT \ln p_i + Z_{iP} \text{ (constant)}$$

where, Z_{iP} is a constant depending on the nature of the gas. It represents the chemical potential of the component when the partial pressure of the component becomes unity.

Since, $p_i = C_i RT$, where C_i is the molar concentration of the component in an ideal mixture, we have,

$$\mu_i = RT \ln C_i + Z_{iC}$$

When N_i denotes the mol-fraction of the i th component in the mixture,*

$$p_i = \frac{n_i}{n_1 + n_2 + \dots} P = N_i P$$

or

$$\mu_i = RT \ln N_i + Z_{iN}$$

Since ideal gas laws can also be extended to ideal dilute solutions, the relations would hold true in the latter cases also. We thus express chemical potential in ideal systems, as

$$\left. \begin{aligned} \mu_i &= RT \ln p_i + Z_{iP} \\ \mu_i &= RT \ln C_i + Z_{iC} \\ \mu_i &= RT \ln N_i + Z_{iN} \end{aligned} \right\} \dots \text{(IV.107)}$$

It must be remembered that the magnitude of the chemical potential (*i.e.*, the partial molal Gibbs potential) would depend upon the composition of the system. The partial molal Gibbs potential of a pure substance obviously will have a constant value independent of the total mass of the substance. It is identical with the molar Gibbs potential of the substance.

It is desirable to mention here a very useful prediction from the Gibbs-Duhem equation. Suppose in a system in equilibrium, a component is present in two phases I and II, having molal thermodynamic potentials G_I and G_{II} . Imagine, at equilibrium, a minute quantity (Δn gm-mole) of the substance passes from phase I to phase II, then by Gibbs-Duhem relation (IV.105),

$$\mu_I (-\Delta n) + \mu_{II} (\Delta n) = \Delta G_{\text{equil.}} = 0$$

or

$$\mu_I = \mu_{II}$$

i.e.,

$$\bar{G}_I = \bar{G}_{II}$$

}

$\dots \text{(IV.108)}$

i.e., The chemical potential (or partial molal thermodynamic potential) of a component in every phase must be the same under conditions of equilibrium.

*If a solution or mixture contains $n_1, n_2, n_3 \dots$ gm-mols of different components, their individual concentrations may be expressed in terms of mol-fractions. Thus, the mol-fraction of

$$\text{1st component, } N_1 = \frac{n_1}{n_1 + n_2 + \dots} = \frac{n_1}{\sum n}$$

$$\text{2nd component, } N_2 = \frac{n_2}{n_1 + n_2 + \dots} = \frac{n_2}{\sum n}$$

$$\text{ith component, } N_i = \frac{n_i}{n_1 + n_2 + n_3 \dots} = \frac{n_i}{\sum n} \text{ and so on,}$$

Thus, in a closed vessel containing a liquid in equilibrium with its vapour, the chemical potentials of water in liquid phase and in vapour phase will be the same, though the masses may be different. Similarly, when iodine remains dissolved in both water and chloroform, which are in contact and in equilibrium, the chemical potential of iodine in the two phases will be the same, though its concentrations in the two phases differ widely.

IV.58. Determination of Partial Molal Quantities. There are quite a number of methods for the determination of the partial molal quantities. We may mention here only one of these methods.

Method of Intercepts. The graphical method of intercepts provides a convenient method for such determination. Consider a solution (or a mixture) containing n_1 and n_2 gm-moles of two components. The suffix (1) will usually denote the solvent. Suppose the partial molal thermodynamic potentials of the components are to be determined. Let y denote the mean thermodynamic potential per gm-mole of the solution, so that

$$y = \frac{G}{n_1 + n_2}; \text{ or } G = (n_1 + n_2)y.$$

At constant temperature and pressure and at constant n_1 , if we differentiate with respect to n_2 , then,

$$\bar{G}_2 = \left(\frac{\partial G}{\partial n_2} \right) = y + (n_1 + n_2) \frac{\partial y}{\partial n_2} \quad \dots (I)$$

The mole-fraction of the solvent is given by, $N_1 = \frac{n_1}{n_1 + n_2}$

$$\text{At constant } n_1, \quad \frac{dN_1}{dn_2} = -\frac{n_1}{(n_1 + n_2)^2} = -\frac{N_1}{n_1 + n_2}$$

We can rewrite (I) above, as

$$\bar{G}_2 = y + (n_1 + n_2) \frac{dy}{dN_1} \cdot \frac{dN_1}{dn_2}$$

$$\text{or} \quad \bar{G}_2 = y - N_1 \frac{dy}{dN_1} \quad \dots (II)$$

Since $\frac{dy}{dN_1}$ is not dependent on the way N_1 is computed, it is no longer necessary to assume n_1 as constant in equation (II)

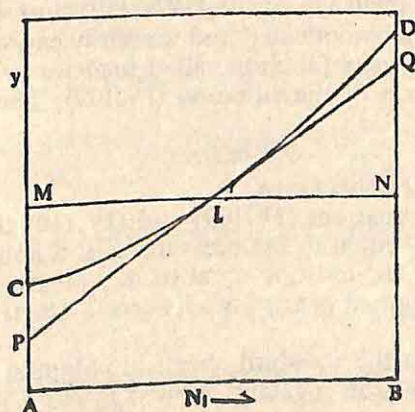


FIG. IV.32 Partial molal quantities from the method of intercepts

The observed mean values of thermodynamic potential per mole, y , are plotted against *mol-fraction* of the solvent N_1 , as the curve CD in Fig. IV.32. Let the point L represent the mol-fraction of the solvent in the solution whose partial property

is to be studied. Draw the line MLN parallel to N_1 -axis and draw the tangent PLQ at the point L . Then the slope at L , is $\tan \angle PLM$, or,

$$PM = N_1 \left[\frac{dy}{dN_1} \right]$$

Hence,
$$\bar{G}_2 = y - N_1 \frac{dy}{dN_1} = AM - PM = AP.$$

Similarly, it can be shown $\bar{G}_1 = BQ$

So, the partial molal quantities of both the components of the solution can be ascertained from the intercepts of the y -axis. The method can be applied in the determination of other partial molal quantities.

IV.59. Fugacity. We have seen that the change in thermodynamic potential is expressed as

$$dG = VdP - SdT$$

For one mole of the substance, the thermodynamic potential is the chemical potential, ($G = \mu$). Then at constant temperature,

$$d\mu = dG = VdP$$

When the system consists of an *ideal* gas, we have

$$d\mu = \frac{RT}{P} dP = RT d \ln P$$

or
$$\mu = RT \ln P + Z_P \quad \dots (IV.107)$$

The constant Z_P depends upon the temperature and nature of the gas. When the gas is at unit pressure ($P = 1$ atmosphere), it is said to be in the standard state and the standard chemical potential, (say) $\mu^\circ = Z_P$. That is,

$$\mu = RT \ln P + \mu^\circ \quad \dots (IV.109)$$

Similar relations will also hold true for the individual components in a mixture of ideal gases. The expression for chemical potentials given in equation (IV.107) is true only for ideal gases.

$$\mu_i = RT \ln P_i + \mu_i^\circ$$

Non-ideal gases. When the system contains a real gas, the relation (IV.109) will not hold true. For, we cannot replace V by $\frac{RT}{P}$ in integrating $d\mu = VdP$.

A suitable equation of state (say, van der Waals') must be used to replace V . Such a procedure leads to a complicated and unweildy expression for μ .

For non-ideal gases, a new function called *fugacity* (f) has been introduced by Lewis retaining the form of the equation (IV.109). The chemical potential is then expressed as,

$$\mu = RT \ln f + \mu^\circ \quad \dots (IV.110)$$

where f is the fugacity of the substance.

Comparison of the equations (IV.109) and (IV.110) shows that for an ideal gas, the fugacity is exactly equal to the pressure. For a non-ideal gas, the fugacity will be a function similar to, but not equal to, the pressure. The factors of non-ideality are therefore contained in the fugacity term. The fugacity is thus a sort of idealised pressure.

It is also obvious that the standard chemical potential will correspond to the state when the real gas has unit fugacity. Now if f_1 and f_2 denote the fugacities of a gas at two pressures p_1 and p_2 , then

$$\mu_2 - \mu_1 = RT \ln \frac{f_2}{f_1} \quad \dots (IV.111)$$

An attempt may now be made to show how the fugacity can be deduced for non-ideal gases. Suppose at a given temperature (T) and pressure (P), the molal volumes

of an ideal and a real gas are V_0 and V respectively. Let the difference between these two be denoted by α . That is,

$$\alpha = V_0 - V = \frac{RT}{P} - V$$

or

$$\alpha dP = RT d \ln P - V dP$$

Hence

$$\alpha dP = RT d \ln P - RT d \ln f \quad [\because V dP = d\mu = RT d \ln f]$$

or

$$\ln f = \ln P - \frac{1}{RT} \int_0^P \alpha dP$$

or

$$\ln \frac{f}{P} = -\frac{1}{RT} \int_0^P \alpha dP \quad \dots (IV.112)$$

$\therefore$

$$f = P e^{\frac{-1}{RT} \int_0^P \alpha dP} \quad \dots (IV.113)$$

Thus we obtain a relation between the fugacity and the pressure. To evaluate $\int_0^P \alpha dP$, the experimentally derived values (from molar volumes) are plotted against P as in Fig. (IV.33) when the area under the curve would give the value of the integrand. The value of the fugacity may then be calculated.

Since at very low pressures f/P tends to unity, i.e., $\ln f/P \rightarrow 0$; α/RT may be plotted against pressure. Integrating this from zero to pressure P we may find the value of f from equation (IV.111).

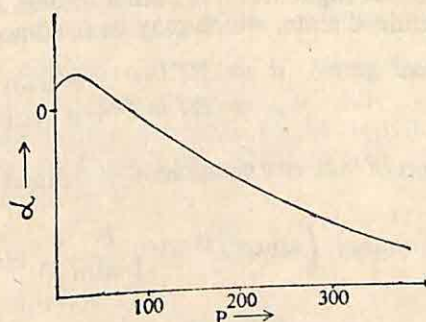


FIG. IV.33

When α is zero, i.e., the gases are ideal, f becomes equal to P . In other words,

$$\left. \begin{aligned} \mu &= RT \ln P + \mu^\circ_{(P=1)}, & \text{for ideal gases} \\ \mu &= RT \ln f + \mu^\circ_{(f=1)}, & \text{for non-ideal gases} \end{aligned} \right\} \dots (IV.114)$$

Example : For oxygen the pressures and fugacities at 0°C are

P (atm)	50	100	200	400
f (atm)	48	92.5	174	338

then the apparent change in thermodynamic potential in compressing 1 mole of O_2 at 0°C from 50 to 200 atmospheres will be

$$\Delta G_{\text{real}} = \mu_2 - \mu_1 = nRT \ln \frac{f_2}{f_1} = 1 \times 1.98 \times 273 \times 2.303 \log \frac{174}{48} = 696 \text{ units.}$$

While under ideal condition, this would have been

$$\Delta G_{\text{ideal}} = \mu_2 - \mu_1 = nRT \ln \frac{P_2}{P_1} = 1 \times 1.98 \times 273 \times 2.303 \log \frac{200}{50} = 498 \text{ units.}$$

IV.60. Activity. We have seen that the determination of fugacities is linked up with gas-pressure. In many cases such determination of fugacities becomes very difficult, as in the case of liquid mixtures or non-volatile substances.

Lewis therefore introduced another function called *activity or relative fugacity*, denoted by 'a'. If f and f° denote the fugacities at a given state and at a standard state arbitrarily chosen, the activity (a) is the ratio of the two fugacities,

$$a = \frac{f}{f^\circ} \quad \dots \text{(IV.115)}$$

(We shall use superscript $^\circ$ to denote the standard state). It means that at the standard state, the activity, $a^\circ = \frac{f^\circ}{f^\circ} = 1$

Since, molal thermodynamic potential $\bar{G}$ or chemical potential (μ) is given by, $\mu = RT \ln f + C$, we have

$$\mu - \mu^\circ = RT \ln \frac{f}{f^\circ} = RT \ln a \quad \dots \text{(IV.116)}$$

where μ° is the chemical potential at the standard state.

In a mixture, for any component i , the partial molal thermodynamic potentials should be taken. Hence,

$$\left. \begin{array}{l} \bar{G}_i - \bar{G}_i^\circ = RT \ln a_i \\ \text{or} \quad \mu_i = RT \ln a_i + \mu_i^\circ \\ \text{[In general : } \mu = RT \ln a + \mu^\circ \text{ (constant)]} \end{array} \right\} \quad \dots \text{(IV.117)}$$

Since the activity is a ratio of fugacities it is dimensionless and its numerical value will depend upon the standard state, which may be fixed according to convenience.

The relations (for real gases) $\mu = RT \ln a + \mu^\circ_{(f=1)}$
and (for ideal gases) $\mu = RT \ln P + \mu^\circ_{(P=1)}$,

prompted the introduction of 'activity coefficient' γ , defined as $\gamma = \frac{a}{P}$ or $a = \gamma P$

where γ is also dimensionless (since $P = \frac{P}{1 \text{ atm}}$). Hence, for real gases, we may write,

$$\mu = RT \ln \gamma P + \mu^\circ \quad \dots \text{(IV.118)}$$

Since for ideal gas $f = P$, i.e., $a = P$, hence $\gamma = 1$.

The deviation of γ from unity for real gases shows directly the extent of non-ideality of the gas, wherein lies its importance.

Solutions. The concept of fugacity and activity has been very profitably extended to solutions. Solutions are regarded as *ideal* when there is no interaction between the components and the physical properties follow additive rules. In such ideal solutions, the vapour pressure of a component over the solution is proportional to its mol-fraction in the solution (Raoult's Law). Thus if P_1 and P_2 denote the vapour-pressures of the two components in a binary solution having mol-fractions N_1 and N_2 , then

$$P_1 = N_1 P_1^0 \quad P_2 = N_2 P_2^0$$

where P_1^0 and P_2^0 are the vapour-pressures of the two components in their pure states at the same temperature. Usually subscript 1 stands for the solvent and subscript 2 for the solute.

Let us now consider one of the components, say the 1st component. Its chemical potential in the vapour phase is

$$\mu_1 = RT \ln P_1 + \mu_1^0 \text{ (assuming ideal behaviour for vapour)}$$

Since the vapour is in equilibrium with the solution, its chemical potential will be the same in the solution phase (eqn. IV.108). That is, in solution also,

$$\mu_1 = RT \ln P_1 + \mu_1^0$$

If we have two solutions in which the same component is present in N_1 and N_1' , mol-fractions with vapour pressures P_1 and P_1' , then

$$\mu_1 - \mu_1' = RT \ln \frac{P_1}{P_1'}$$

It is now necessary to choose a standard state, which for a liquid (or a solvent) is often taken as its pure state (vap. pressure P_1°). We may then write

$$\mu_1 - \mu_1^\circ = RT \ln \frac{P_1}{P_1^\circ} \quad \dots \text{(IV.119)}$$

When the solutions are ideal, we can introduce Raoult's Law, so that

$$\mu_1 - \mu_1^\circ = RT \ln \frac{N_1 P_1^\circ}{P_1^\circ} = RT \ln N_1 \quad \dots \text{(IV.120)}$$

In real solutions, we shall see later, there is considerable deviation from the Raoult's Law and the equation (IV.119) is not valid. As in the case of gases, retaining the form of expression for ideal solutions we may replace the vapour pressures by fugacities in dealing with non-ideal solutions, so that

$$\mu_1 - \mu_1^\circ = RT \ln \frac{f_1}{f_1^\circ}$$

when f_1° is the fugacity of the component in the standard state and f_1 in the given state.

Defining, as in the case of gases, activity by $a_1 = \frac{f_1}{f_1^\circ}$, we have

$$\text{for non-ideal solutions, } \mu_1 - \mu_1^\circ = RT \ln a_1 \quad \dots \text{(IV.121)}$$

$$\text{and for ideal solutions, } \mu_1 - \mu_1^\circ = RT \ln N_1 \quad \dots \text{(IV.120)}$$

When the real solution is extremely dilute, it tends to behave ideally, so that $a_1 \rightarrow N_1$. At higher concentrations, the ratio of the activity to the concentration, (a_1/N_1), deviates considerably from unity. This ratio of activity to the concentration is the *activity coefficient*, γ_1 or

$$\gamma_1 = \frac{a_1}{N_1}$$

For solutions which are non-ideal,

$$\mu_1 = RT \ln a_1 + \mu_1^\circ = RT \ln \gamma_1 N_1 + \mu_1^\circ \quad \dots \text{(IV.122)}$$

In general, for any component of the solution,

$$\mu = RT \ln \gamma N + \mu^\circ \quad \dots \text{(IV.123)}$$

If the concentration be expressed in molar units instead of the mol-fractions, the chemical potential μ is written as,

$$\mu = RT \ln fc + \mu^\circ \quad \dots \text{(IV.124)}$$

where f is the activity coefficient and c is the molar concentration of the component in solution.

Example : An aqueous solution of alcohol, in which mol-fraction of alcohol is 0.05 gave partial pressures of water and alcohol as 23.2 and 10.8 mm respectively. The vapour pressures in the pure state are $p_{\text{alc}} = 21.76$ mm. and $p_{\text{water}} = 23.8$ mm. at the same temperature. Then

$$\text{activity of water } a_1 \approx \frac{p_1}{p_1^\circ} = \frac{23.2}{23.8} = 0.98$$

$$\text{activity of alcohol } a_1' = \frac{p_1'}{p_1'^\circ} = \frac{10.8}{21.76} = 0.49$$

$$\text{activity coeff. of water} = a_1/N_1 = 0.98/0.95 = 1.03$$

$$\text{activity coeff. of alcohol} = a_1'/N_a = 0.49/0.05 = 9.8.$$

REFERENCES FOR FURTHER READING

- (i) Thermodynamics : Zemansky
- (ii) Modern Thermodynamics : Guggenheim
- (iii) Thermodynamics and the free energy : Lewis & Randall
- (iv) A Treatise on heat : Saha & Srivastava
- (v) Chemical Thermodynamics : Klotz
- (vi) Thermodynamics for chemists : Glasstone

Problems

1. Calculate the work involved in the following processes :

- (a) At a constant pressure of 1 atm. two moles of an ideal gas are heated from 27°C to 127°C . [Ans : 16.4 lit-atm.]
- (b) Under 1 atm. the density of water is 0.9998 gm/c.c. at 0°C and 0.9584 gm/c.c. at 100°C . One mole of water is heated under 1 atm. from 0°C to 100°C . [Ans : 7.4×10^{-4} lit-atm.]
- (c) At 0°C and 1 atm. 45 gms of ice melt into liquid water. The decrease in volume per mole during fusion is 1.48 c.c. [Ans : -3.7×10^{-3} lit-atm.]
- (d) One gm-atom of zinc dissolves at the negative electrode in a Daniel cell of e.m.f. 1.1 volt. [Ans : 212300 joules.]
- (e) At 25°C and 1 atm. a gm-mol of BaCO_3 dissociates as $\text{BaCO}_3(s) \rightarrow \text{BaO}(s) + \text{CO}_2(g)$. [Ans : 24.4 lit-atm.]

2. The molar heat of vaporisation of $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ is 9700 cal. at 100°C . Evaluate ΔU per mole at 100°C and 1 atm. The molar volume of liquid and of vapour are 18 c.c. and 30.2 litres at 100°C and 1 atm. [Ans : 8975 cal.]

3. 100 gm Argon is allowed to expand from a pressure of 10 atm. to 0.1 atmosphere at 100°C . Calculate the heat which is absorbed assuming ideal behaviour. [Ans : 8580 cal.]

4. Isothermally at 127°C a gm-mole of nitrogen, which obeys Van der Waals equation, expands from a volume of 10 litres to 1 litre. What will be amount of work done, if $a = 1.39$ atm-litre²/mole² and $b = 0.039$ litre/mole?

5. 5.6 gm of nitrogen is adiabatically compressed from 10 to 5 litres, calculate the final temperature and also the work done on the gas. $C_P = \frac{7}{2}R$.

6. Two litres of CO_2 at 0°C and 5 atm are expanded isothermally until the pressure is 1 atmosphere. Assuming the gas to be ideal calculate ΔW , Δq , ΔU and ΔH for the process.

Also find out these values if the process were effected adiabatically.

7. A gm-mole of an ideal gas ($C_V = 8.0$ cal) was initially at 0°C and 10 atm. The external pressure is suddenly reduced to 1 atm. and the gas expands adiabatically against this pressure. What is the final temperature? Final volume? [Ans : 218°K , 17.9 litres.]

8. At 20°C , we have a gm-mole of an ideal gas ($C_P = 8.6$) at 15 atm. What will be the final volume and temperature if

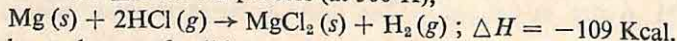
(i) it expands adiabatically against a constant pressure of 5 atm.

(ii) it expands adiabatically from 15 atmospheres to 5 atmospheres? Calculate also ΔW and Δq in each case.

9. At low temperatures a non-ideal gas follows the relation $PV = RT + a/V$, where the cohesive pressure constant, $a = 3.6$ atm.-litre²/mole². Calculate the work done by one mole of this gas in expanding from 0.224 litres to 22.4 litres at 127°C . Compare this result with the work done in corresponding expansion of an ideal gas. [Ans : 4034 cal.]

10. The pressure of a gas is represented by $p = 20/V$ (atm.) where V is the volume of the gas. If the gas expands from 5 to 50 litres and undergoes an increase in internal energy by 200 cal, how much heat will be absorbed during the process? [Ans : 1322.4 cal.]

11. Evaluate ΔU for the process (at 500°K),



The volume-change of solids may be ignored.

12. The heat-capacities at constant pressure for CO , CO_2 and O_2 are $C_P(\text{CO}) = 6.97$, $C_P(\text{CO}_2) = 8.97$, $C_P(\text{O}_2) = 7.0$. The standard heat of reaction for the process $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$; is $\Delta H_{298} = -67650$ Cal. Find out ΔH of the process at 100°C . [Ans : 67762.5 cal.]

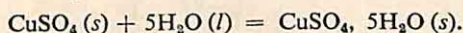
13. Calculate the enthalpy of vaporisation of SO_2 at -25°C if the same at its boiling point (-10°C) be 5950 cal/mole. Given the molar heat capacities

$$C_{P(l)} = 20.6 \text{ cal/mole, } C_{P(g)} = 9.3 \text{ cal/mole.}$$

[Ans : 6119.5]

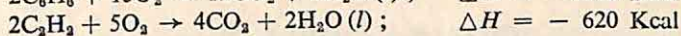
14. The heat of combustion of C_2H_5OH at $20^\circ C$ and 1 atm. is -238 Kcal. Calculate its heat of formation (use tables of standard data).

15. The heat of solution of anhydrous $CuSO_4$ and of $CuSO_4 \cdot 5H_2O$ are -15800 cal and 2750 cal per mole. Find the heat of hydration in



16. The heats of formation of $Na_2B_4O_7(s)$ and $Na_2B_4O_7 \cdot 10H_2O(s)$ are -742 and -1460 Kcal respectively. Calculate the heat of hydration of $Na_2B_4O_7$ in forming the decahydrate.

17. At constant volume at $27^\circ C$



Calculate the heat of polymerisation of acetylene to benzene at constant pressure. [Ans : -131.2 Kcal]

18. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are

$$\Delta H_{fH_2O(l)} = -68320 \text{ cal}$$

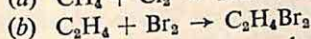
$$\Delta H_{fCO_2(g)} = -94050 \text{ cal}$$

The heat of combustion of methyl alcohol is -173.65 Kcal. Calculate the heat of formation of liquid methyl alcohol.

19. The heat of neutralisation of $HCN(aq)$ is 3000 cal at a constant pressure at $25^\circ C$. What is the heat of dissociation of HCN ?



20. Evaluate, from bond energy values, the heat of gaseous reaction,



[Use the bond-energy values from the table.]

21. At $17^\circ C$, the heat of combustion at constant pressure of amorphous carbon is 96960 cal, that of CO to CO_2 is 67960 cal. Determine the heat of formation of CO at constant volume.

[Ans : -29290 cal.]

22. The available heat from burning a fuel is 8000 cal/gm. What is the maximum work that can be obtained from it when the engine works between boiling pt. of water and $30^\circ C$? What is the efficiency of the engine?

[Ans : $\eta = 0.19$]

23. Calculate the entropy-change in

(a) Vaporisation of ether [$L = 6500$ cal/mole, b. pt = $35^\circ C$]

(b) Compressing 20 gms of helium from a pressure of 1 to 10 atmospheres at $20^\circ C$.

[Ans : (a) 21.1 e.u. (b) -23.0 e.u.]

24. Calculate in calories per degree the difference in entropy of

(a) 1 mole of water vapour at $100^\circ C$ and 1 atm. and 1 mole of water at $100^\circ C$ & 1 atm.

(b) 1 mole of water (l) at $100^\circ C$ and 1 atm. and 1 mole of water (l) at $25^\circ C$ and 1 atm.

(c) 1 mole of water vapour at $100^\circ C$ and 0.1 atm. and 1 mole of water vapour at $100^\circ C$

and 1 atm. [$C_p(H_2O, g) = 9$ cal/mole, $C_p(H_2O, l) = 18$ cal/mol]

25. The heat capacity for nitrogen is 7 cal per mole per degree. What will be entropy-change if 7 gms of the gas be heated from $300^\circ K$ to $500^\circ K$ at (i) constant volume and (ii) at constant pressure?

[Ans : (i) 0.633 (ii) 0.8855 e.u.]

26. For NH_3 , $C_p = 6.2 + 7.9 \times 10^{-3} T$ cal/mole-degree. Assuming ideal behaviour, estimate the entropy-change in heating 34 gms of the gas from a volume of 100 litres at $300^\circ K$ to a volume of 60 litres at $800^\circ K$.

27. What is the change in entropy (a) if 200 gms of water at $27^\circ C$ be mixed with 500 gms of water at $57^\circ C$ (b) if 100 gms of ice ($0^\circ C$) be added to a Kg of water at $25^\circ C$ in an isolated system?

[$L_{ice} = 1435$ cal, $C_p H_2O = 18$ cal.]

28. One mole of Helium and one mole of hydrogen are mixed at a const. temp. What will be the entropy-change?

29. The van der Waals constants for CO_2 are $a = 3.59$ litre²-atm/mole² and $b = 0.043$ litre/mole. Evaluate the J-T coefficient of the gas at $0^\circ C$. What is the inversion temperature of this gas?

30. Five moles of an ideal gas are compressed isothermally and reversibly at $27^\circ C$ from a pressure of 10 atm. to 20 atm. Calculate the change in Gibbs potential for the process. Also find out ΔU , ΔH , ΔS and ΔW .

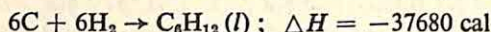
[Ans : $\Delta G = 2070$ cal.]

31. For a reaction at 127°C,

$$\Delta G = -12 \text{ Kcal and } \Delta H = -17.5 \text{ Kcal}$$

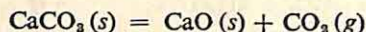
$$\text{Find out } \Delta S \text{ and } \left[\frac{\partial(\Delta G)}{\partial T} \right]_p.$$

32. At 25°C, the entropy of cyclohexane (l) is 49.3 cal/degree and the heat of its formation,



Calculate the free energy of its formation from the elements at 25°C.

33. The entropy change in the decomposition of calcium carbonate under standard conditions is 38.4 e.u.



What is the standard entropy of $CaCO_3$? (use tables)

[Ans : 22.2]

34. What is the approximate boiling point of water at a place where the atmospheric pressure is 600 mm?

35. Calculate the change in the m.pt of ice brought about by the application of 100 atm. pressure. The volume change on melting is
- -1.63×10^{-3}
- litre/mole and the enthalpy of fusion is 1440 cal/mole.

[Ans : $\Delta T = -0.75^\circ$]

36. The densities of solid and liquid phenol (m.pt. 41°C) are 1.072 and 1.056 gm/c.c. respectively. Estimate the change in m.pt. if the pressure be raised to 10 atm. [
- $L^* = 25$
- cal/gm.]

37. The transition point of
- α
- to
- β
- sulphur is 96.6°C. The specific volumes of
- α
- and
- β
- sulphur are 0.495 and 0.505 c.c. respectively. The heat of transition is 75 cal/gm-atom. What will be the transition temperature at 25 atm. pressure.

38. The heat of vaporisation of cyclohexane (b.pt. 80°C) is 85 cal/gm. The specific densities of liquid and vapour are 0.72 and 0.003 gm. at this temperature. Find out the pressure at which the liquid can be distilled at 30°C.

39. Find out the value of
- ΔG
- per mole at
- -10°C
- for



Given $C_P (H_2O, s) = 9$ cal/mole, $C_P (H_2O, l) = 18$ cal/mole, $\Delta H_{273} = 1440$ cal/mole.

[Ans : $\Delta G = -54$ cal/mole]

40. At 25°C, the e.m.f. of a galvanic cell
- $[Ag(AgCl) - HCl - H_2]$
- was found to be 0.233 volts. When the chemical process occurring in the cell is carried out in a beaker, the heat of reaction
- $\Delta H = -17400$
- cal/mole of
- H_2
- . Calculate the maximum work available from the process in the galvanic cell. What energy is used for operation of the cell?

[Ans : $W_{\max} = 10.7$ Kcal. ; $q = -6.7$ Kcal.]

THE STRUCTURE OF THE ATOM

A. ELECTRON

V.1. Dalton's atomic theory should be regarded as the primary basis of chemistry as it grew up in the last century. Chemistry rests largely on this theory which clearly explains the observed quantitative laws of chemical reactions. But Dalton's concept of indivisibility of the atom is, however, discarded by the discovery of various fundamental particles like proton, neutron, electron, etc, which constitute atoms of all elements. The idea about these particles resulted really from Faraday's famous work on electrolysis (1834).

Faraday made an intensive study of the decomposition of solutions of salts, acids and bases by the passage of electric current. From these researches, he established the quantitative relations between the amount of electrolysis and the quantity of electricity. These relations are embodied in the well-known *Faraday's Laws of Electrolysis*, which indeed form a keystone of chemistry. It was soon realised that the current was conveyed in the solution by charged particles or ions. Further it was found that one gm-equivalent of any element was deposited or dissolved by 96490 coulombs or one faraday ($\mathcal{F}$) of electricity. The far-reaching significance of this discovery was first pointed out by von Helmholtz in 1881. Suppose we consider an element having valency n . Since one gm-equivalent is discharged by $\mathcal{F}$, one gm-atom will correspond to $n\mathcal{F}$ faradays of electricity. This amount of electricity ($n\mathcal{F}$) is nothing but the charge borne by a gm-atom in its ionic state. A gm-atom carries a charge $n\mathcal{F}$, in which n is a whole number. The ionic charges of all elements are therefore integral multiples of a certain unit since the number of individual atoms in 1 gm-atom is the same N_0 (Avogadro number). A single ion therefore carries a charge which must be an integral multiple of $\mathcal{F}/N_0$. This means that the electricity is also atomic in character. This idea of atomicity of electricity was firmly corroborated from the study of the ionisation of gases.

V.2. The Discharge of Electricity through Gases. It was known for a long time that gases at very low pressures, if subjected to high potential, become conducting and various luminous effects were observed. A typical apparatus to study these properties is shown in Fig. (V.1). It consists of an elongated tube closed at both

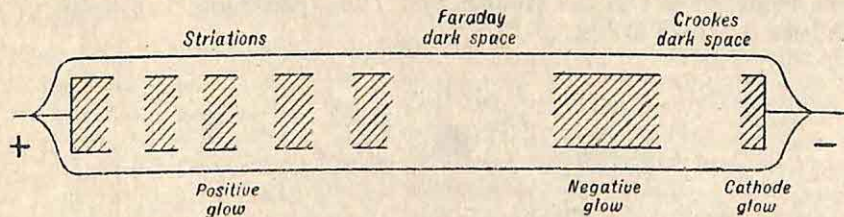


FIG. V.1 Electric discharge tube

ends. Two metal electrodes are sealed inside at the two ends and there is a side-tube connected to a pumping system to reduce the pressure. If we take air inside and reduce the pressure to 1 mm (say) and apply a high potential the tube will be filled up with a reddish glow. On further reducing the pressure, say to 0.1 mm, there will be a fine glow around the cathode then a dark space called the *Crookes dark space*, then another glow (negative glow) followed by *Faraday dark space*. The rest of the tube will show the striations of positive glow up to the anode. The arrangement of the dark-spaces and glows varies with pressure,

When the pressure is much lowered (say, 0.001 mm), the Crookes dark space extends and fills up the entire tube. In such conditions, a streak of rays, named *cathode rays*, emanate from the cathode and when they impinge on the opposite walls they produce a fluorescence there. The cathode rays have been very carefully studied. They show many definite characteristics.

The cathode rays, as just mentioned, excite fluorescence on the glass walls where they impinge. The rays travel in straight lines. This is confirmed by the shadows formed when objects are placed in their path. The cathode rays have a penetrating power and can pass through very thin metal foils. The rays are able to heat bodies by impact. They also possess a considerable momentum ; small paddle wheels placed in their path, at very low pressures, would begin to rotate.

The cathode rays are deflected from their original path by the application of a magnetic or an electrostatic field. It means that the rays are associated with electric charge. From the direction of deflection, it is found that the charge accompanying the rays is a negative one.

When the rays are allowed to impinge on matter, a different type of new radiation, called *X-rays*, is produced. Usually, a metal target, called *anti-cathode*, is suitably placed in the path of the cathode rays (Fig. V.2) when X-rays are emitted.

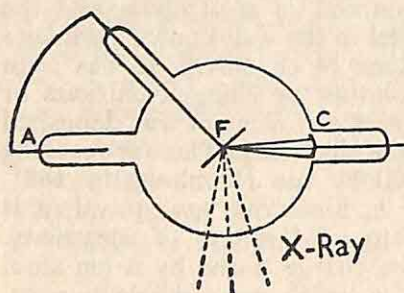


FIG. V.2 X-rays

The X-rays also are highly penetrating ; they are capable of ionising gases ; they can excite fluorescence on substances like zinc sulphide. But X-rays are not deflected in a magnetic or electrostatic field showing that they do not carry charges. In fact, these are electromagnetic waves, like light waves, but of very short wave-lengths. Apart from the various general applications, the X-rays were of great help in the determination of the atomic structure and the crystal structure.

It is necessary to mention here that another kind of rays is also present in the cathode-ray tube. These rays seem to flow from the direction of the anode towards the cathode and if the cathode is a perforated one, they pass out through the cathode holes and are called *positive rays* or *canal rays*.

The cathode rays were found to consist of charged material particles and are deflected by magnetic and electrostatic fields. That the cathode rays really consist of streams of negatively charged particles, called *electrons*, was first successfully established by J. J. Thomson (1897). He was the first to measure the ratio of the charge to the mass of the electron (e/m).

V.3. Determination of e/m of Cathode rays. The experimental arrangement devised by Thomson is shown in Fig. (V.3).

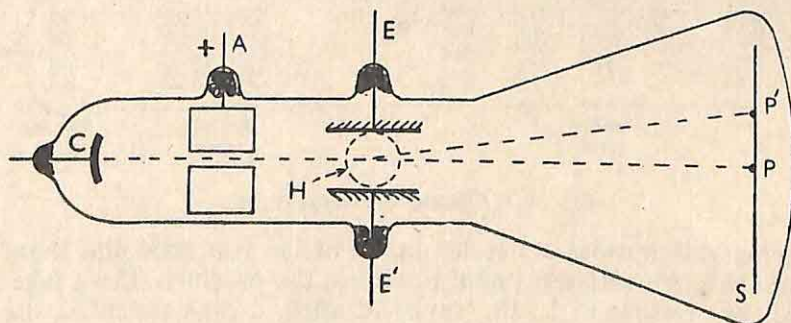


FIG. V.3 Determination of e/m (Thomson)

A narrow beam of cathode rays emitted from a circular disc cathode C is allowed to pass through a narrow slit of the cylindrical anode A, along the axis of the cathode-ray tube. The pencil of cathode ray ultimately strikes a zinc-sulphide

screen S producing a fluorescent spot at P . Two parallel metal plates E, E' are placed inside the tube such that the beam passes in between them. A difference of potential say, V , is applied to the plates E, E' , when the ray is deflected and the fluorescent spot shifts from P to P' . Subsequently, a magnetic field H , produced by an electromagnet (shown by dotted circle) is also applied. The magnetic field will also deflect the beam. Applying the magnetic field perpendicular to the electric field and acting in a direction such that the deflection of the beam is opposite, the fields are so adjusted as to keep the beam in its original path, *i.e.*, the fluorescent spot P does not alter. Suppose the mass, velocity and the charge carried by a particle are m, v and e , then the magnetic force acting on the particle is Hev and this is equal to the centrifugal force mv^2/r .

$$\text{Hence,} \quad Hev = \frac{mv^2}{r} \quad \dots (i)$$

Again, if X be the electric field, the electric force is Xe , so that, under the conditions noted above,

$$Hev = Xe, \quad \text{i.e., } v = X/H \quad \dots (ii)$$

Substituting (ii) in (i), we have,

$$e/m = X/H^2r$$

where r is the radius of curvature of the path of the cathode ray beam under the magnetic field H and can be measured.

The value of e/m obtained by Thomson was 1.76×10^7 emu/gm. Several other methods were applied and always the same value was found. Whatever the gas through which the cathode rays pass and whatever the material of the cathode from which they radiate, the ratio of the charge to mass is the same for all cathode rays. Measurements of e/m with electrons from other sources, such as emitted from hot filaments etc., gave practically the same value. This confirmed that the electrons formed a universal constituent of all forms of matter.

The recent accurately determined value of e/m for an electron is

$$\begin{aligned} e/m &= 5.27 \times 10^{17} \text{ esu per gm} \\ &= 1.76 \times 10^{11} \text{ coulomb per kilogram.} \end{aligned}$$

From Faraday's laws of electrolysis, we can obtain the charge associated with unit mass of hydrogen in the ionised state. Are the electrons identical with charged hydrogen atoms except that the charge is opposite? A comparison of the e/m -values would be interesting. For hydrogen ion, the e/m value is about $1/1836$ of that of a cathode ray particle. Either the charge carried by a hydrogen ion is $1/1836$ times less than that of an electron or the mass of the hydrogen atom is nearly 1836 times greater than that of the electron, the latter being the most reasonable explanation. But the final confirmation may come only from the direct determination of the charge.

V.4. The Charge of the Electron. In 1896 Wilson had shown that if ions are present in an atmosphere saturated with water vapour fine droplets of water condense on the ions, *i.e.*, the ions act as nuclei for the condensation of the water droplets. This was utilised by Townsend and by Thomson in measuring the charge of the electron. Ions were produced in a gas stored over water by the passage of X-rays. A cloud of droplets was then formed by sudden expansion and cooling of the gas. It was presumed that every droplet was associated with only one ion, *i.e.*, one charge and the conditions favoured condensation only on the negative charges. It was necessary to determine the number of droplets and also the total charge carried by the condensed cloud. By measuring the velocity of fall of the droplets in air and by applying Stoke's Law, the average size of the drops was determined. The total weight of the precipitated water was then determined from which the number of droplets was found out. For ascertaining the total charge carried by the cloud, the charged droplets were collected in a quadrant electrometer. It was estimated that the value of the unit negative charge, $e = 6.5 \times 10^{-10}$ esu. In spite of the liberal assumptions involved and the difficulties of experiment, the result obtained from their experiments was quite good. An accurate deter-

mination was rendered possible by Millikan during the years 1909—1916, by using a more refined method.

Millikan's Experiment. A diagrammatic sketch of Millikan's apparatus is given in Fig. (V.4). It consisted of a cylindrical vessel *B*, placed in a constant-temperature bath. Inside *B* there were two parallel brass plates *X* and *Y*, *X* being connected to a known steady high potential (say 5000~10000 volts) and *Y* being earthed. There was a pin-hole at the centre of the charged upper plate *X*. The pressure inside was controlled by a pump and a manometer. 'A' was an atomiser through which very fine droplets of an oil could be injected into the vessel. Two windows *W*, *W* were fitted to the vessel in the opposite walls, in the same line as the parallel plates. Through one window, a momentary beam of X-rays was introduced to ionise the gas in between the plates; a telescope-eyepiece provided with a scale was placed at the other window. The space between the plates was kept illuminated by a light beam from which the thermal rays were cut off by filters.

A droplet of oil, usually positively charged due to friction, sometimes during its sojourn, entered through the pin-hole of the plate *X* and came into view of the eyepiece. Its exact position at any moment could be easily ascertained with the help of the scale in the eyepiece. The droplet, after entering, moved downwards towards *Y*, but the field was then applied by charging the upper-plate *X* and the drop would begin to rise towards *X*. When the droplet almost reaches *X*, the field was switched off and the droplet would move downwards under gravity until it would almost reach *Y*, when the field was again applied causing the droplet to move up. In this way, a droplet was moved up and down many times, sometimes several hundred times.

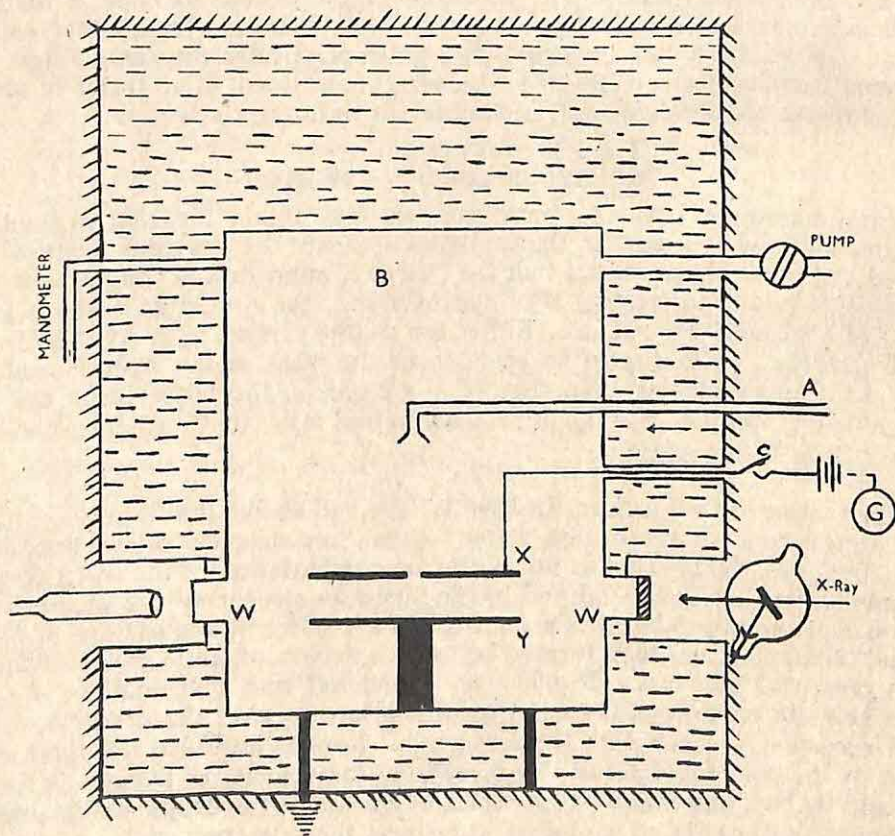


FIG. V.4 Millikan's apparatus

It was found that the droplet while falling under gravity, took always the same time, namely 13.595 seconds to cover a distance of 0.5222 cms. The time was recorded with the help of a high-precision chronograph. But while moving

upwards, the droplet needed different time on different journeys under the same field (5051 volts). That is, its velocity upwards varied from time to time. Obviously, the charge on the droplet must have altered. A sample of the time-records would be illustrative.

Serial No. of journey upwards	Time in seconds (5051 volts, $d=0.5222$ cms)
1	12.5
2	12.4
3	21.8
4	34.8
5	84.5
6	84.5
7	85.5
8	34.6
9	34.8
10	34.8
11	34.6
12	21.9

It is evident during the first and second trips upwards the charge on the droplet remained constant. On the third journey up, the rate was slow, the droplet must have picked up a negative ion. In the fourth and fifth upward journeys, more time was needed indicating further addition of negative charges. During the sixth and seventh trips, the charge remained constant. But in the eighth trip upward, the velocity suddenly increased indicating that the droplet must have taken up a positive ion. Now, say,

x_1 = velocity under gravity alone.

x_2 = velocity under gravity and the field of strength (say) E .

Then, $x_1/x_2 = mg/(Ee - mg)$

where e , the charge carried by the droplet of mass m .

Hence,
$$e = \frac{mg}{Ex_1} (x_1 + x_2)$$

Since all the quantities on the right-hand of this equation were known, the value of e was easily determined.

Suppose x_3 was the velocity in the third upward trip ($t = 21.8$ secs) and x_4 was the velocity in the fourth trip ($t = 34.8$ secs) when the droplet had taken up an additional charge, then

$$e_3 = \frac{mg}{Ex_1} (x_1 + x_3) \quad e_4 = \frac{mg}{Ex_1} (x_1 + x_4)$$

$$\text{or the additional charge} = \frac{mg}{Ex_1} \times 0.5222 \left[\frac{1}{21.8} - \frac{1}{34.8} \right]$$

Putting the values of E , mg , x_1 ... etc., the magnitude of this additional charge was found to be 4.77×10^{-10} esu. (The mass of the droplet is determined from its velocity under gravity by applying Stoke's law).

When successive values of x_4 , x_5 , x_6 ... etc., were put in the above equations, the value of the charge captured by the droplet was always practically the same i.e., $(4.775 \pm 0.005) \times 10^{-10}$ esu. This value did not depend upon the number of trips or on the nature of the gas ionised or oil-drop used, nor did it vary with pressure. This confirms the atomic nature of electricity. The magnitude of the charge of the electron, as recently determined, is

$$\begin{aligned} e &= 4.802 \times 10^{-10} \text{ esu} \\ &= 1.602 \times 10^{-19} \text{ coulomb.} \end{aligned}$$

Since we know, for an electron, $e/m = 5.27 \times 10^{17}$ esu/gm.

$\therefore$ the mass of the electron, $m = 4.8 \times 10^{-10} / 5.27 \times 10^{17} = 9.1 \times 10^{-28}$ gms.

The energy of the electron is e^2/r , where r is the radius. Assuming the entire mass is electromagnetic, we have

$$E = mc^2, \text{ i.e., } e^2/r = mc^2$$

$$\therefore r = e^2/mc^2 = \frac{(4.8 \times 10^{-10})^2}{9 \times 10^{-28} \cdot (3 \times 10^{10})^2} = 2.8 \times 10^{-13} \text{ cms.}$$

The electron is indeed very small in mass and size.

B. RADIOACTIVITY

V.5. The history of atomic chronicle must also include another great discovery, namely, the phenomenon of radioactivity. In 1896 the French scientist Becquerel, while investigating the nature of mysterious X-rays discovered by Rontgen a few months earlier, found that a photographic plate wrapped in thick black paper was affected by a sample of potassium-uranyl-sulphate placed over it. In fact, any uranium compound would affect the plate though covered by paper and kept away from light. The obvious conclusion was that some radiations emanating from the uranium compound could penetrate through the cover and attack the photographic plate. This penetrating radiation had its source in uranium itself and Becquerel christened this amazing behaviour as 'radioactivity'. The properties of these radiations were very similar to those of X-rays. They were highly penetrating, they affected photographic plates, they would ionise gases and would also induce fluorescence in some substances. The rays are not influenced by heat, light or chemical composition. The property of ionising gases and making them conducting became helpful in detecting and estimating them quantitatively. The rate of discharge of a gold-leaf electroscope by the air ionised by these radiations was a measure of their intensity. By applying this device, Marie Curie found that the activity of mineral pitchblende was far greater than what was expected of its uranium content. In 1898 Pierre and Marie Curie actually isolated two new elements—polonium and radium—which were more radioactive compared to uranium, the heaviest atom known at the time. Soon after other radioactive substances were discovered, amongst them thorium, the second heaviest atom of the time. In 1900, Debierne and Giesel discovered actinium which was also radioactive. That the radioactive effects were essentially atomic was recognised early and this helped the isolation to a considerable extent. It was immaterial how uranium or radium was chemically combined. The same number of radium atoms will always have the same activity independent of the physical state or the environmental conditions.

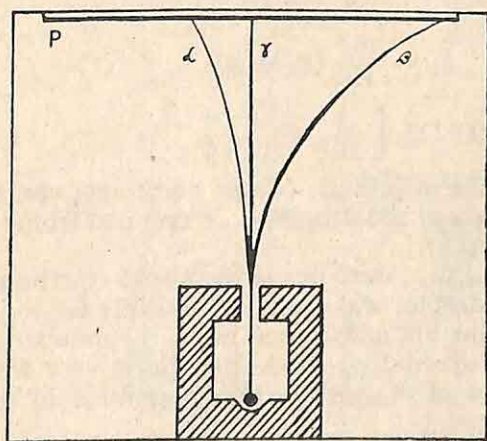


FIG. V.5

V.6. Radiations from Radioactive Substances. In the radiations emanating from radioactive substances, three different kinds of rays have been found, *alpha*-, *beta*-, and *gamma*-rays. Of these, α - and β -rays are deflected in magnetic and electrostatic field indicating that they consist of charged particles. The γ -rays are wave motions of very small wavelengths (like X-rays) and are not affected by magnetic or electric fields. This difference can be very easily shown by a simple experiment, similar to that originally done by Becquerel and others. In a deep groove in a block of lead, a minute quantity of

a radioactive sample is taken (Fig. V.5). The lead block is kept in an evacuated chamber and a photographic plate (P) is fixed on the wall of the chamber opposite to the open end of the groove. Now a strong magnetic field at rt. angles to the plane

of the paper and in a direction away from the reader is applied, when α -rays are deflected to the left, β -rays to the right and γ -rays remain undeviated, producing dark images in the plate.

α -rays. That the α -rays consisted of positively charged particles was immediately known from the nature of the deflection in a magnetic field of a given direction. The magnitude of e/m , ratio of charge to mass, of the α -particles was next determined by the same technique as applied in the case of cathode particles. For α -particles, the value of e/m was found to be 4820 emu/gm.

To ascertain the charge or the mass of these particles further experiments were necessary. The charged particles can produce a scintillation or flash when they strike a zinc-sulphide screen. The number of flashes correspond to the number of α -particles. By this method, called the scintillation method, the number of α -particles shot out from a given sample in vacuum through a narrow slit in a given time was counted.

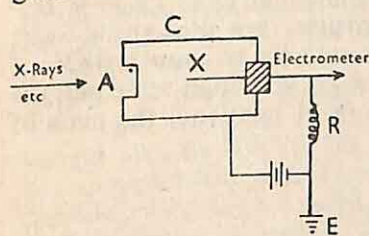


FIG. V.6 Geiger counter

There is also an alternative method of determining the number of α -particles with the help of a Geiger counter (Fig. V. 6). In a cylinder containing air at low pressure (say 5 cms), a wire 'X' is mounted parallel to the axis of the cylinder. A potential is maintained between X and the cylinder walls. Through a thin Mica window A, the alpha particles enter and ionise the gas

inside. An ionisation current is set up and there is a momentary swing in an electrometer connected to X. From the swings in the electrometer, the α -particles entering the cylinder in a given time are counted. Rutherford and Geiger found that 3.57×10^{10} α -particles were emitted per second from one gram of radium.

Next the total charge carried by the α -particles per unit time was determined by replacing the zinc-sulphide screen with a metal plate connected to an electrometer. The charge carried by one α -particle was thus found to be 9.3×10^{-10} esu. Hence the charge carried by an α -particle is twice the electronic charge, i.e., an α -particle carries two units of positive charge.

Since e/m was known, the mass of an α -particle was easily computed and found to be 6.6×10^{-24} gms. The mass of a hydrogen atom is really 1.67×10^{-24} gms, hence an α -particle is four times as heavy as a hydrogen atom. We further know that the helium atom is also 4 times heavier than a hydrogen atom. This led to the inference that an α -particle was a doubly-charged helium atom, a conclusion which was experimentally established by Rutherford and Royds (1909). An apparatus as in Fig. V.7 was used for the purpose. In a thin-walled tube A, a quantity of radioactive gas radon was taken. A wider thick-walled glass-tube B, projecting upwards into a sealed capillary end tube C, surrounded A. The air from B and C was pumped out and the apparatus allowed to stand for a few days. The α -particles emitted from radon passed out through the thin walls of A and entered B. The gas volume in B was compressed by introducing mercury through a side-tube when α -particles accumulated in C. An electric discharge between two electrodes (already sealed in C) was passed and the spectrum of the discharge was identified to be that of Helium. This confirmed that α -particles were charged helium atoms.

The α -particles are emitted with high velocities (1.6×10^9 cms/sec). The mass is also relatively large. It thus possesses high kinetic energy. The kinetic energy

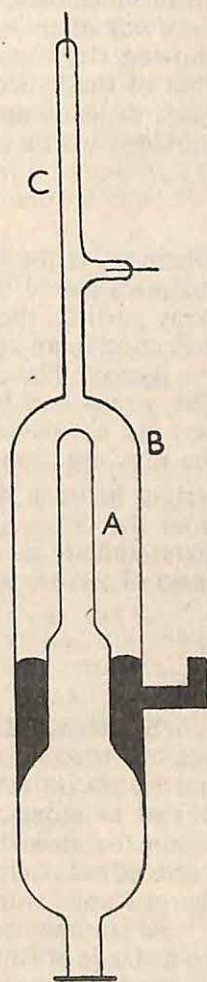


FIG. V.7 Detection of Helium from α -particles

of an α -particle from Radium C is about 1.2×10^{-5} ergs, i.e., 7.7 electron-volts. Because of the high energy content, the α -particles have great ionising power. The penetrating power of α -particles is smaller than β - or γ -rays. The α -particles are stopped by a sheet of lead 1 mm thick, β -rays easily pass 3 mm thickness of lead and γ -rays 15 cms of lead.

β -rays. The easy deflection of these rays in a magnetic or electrostatic field and also the identification of the charge delivered by them to an electroscope proved β -rays consist of negatively charged particles. These differ from the α -particles also in their greater penetrating power. These also affect photographic plates and possess the power of ionising gases though not as strongly as the α -particles.

Kaufmann (1902) carefully measured the e/m ratio and also velocity of these particles. He found that e/m value was the same as that of the cathode particles. The velocity of the β -particles was found to vary depending upon the source from which these are emitted. Usually the velocity is quite high ($2.83 \sim 2.36 \times 10^{10}$ cms/sec) often approaching that of light. The β -particles are thus really swift moving electrons. The mass of an electron of low velocity is about $1/1836$ of that of the hydrogen atom. For a particle moving with very high velocities, the mass depends upon the velocity. Applying the theory of relativity, the mass of moving electron (m) will be given by

$$m = m_0 \left[1 - (v/c)^2 \right]^{-\frac{1}{2}}$$

where m_0 is the rest mass, v = velocity of electron, c = velocity of light. Thus the mass would be infinite if it moves with the velocity of light. For an ordinary β -ray particle, the kinetic energy is less and so its ionising power is less and their deflection in an applied electric field is also easier.

γ -rays. The γ -rays have much greater penetrating power than α - or β -rays. The γ -rays can be detected even after passing through 30 cms of iron. These rays are not deviated by a magnetic field and therefore carry no charge. In fact, the rays are electromagnetic waves of very short wavelengths ranging approximately between $4 \text{ \AA}$ to $0.04 \text{ \AA}$. They are thus comparable to X-rays and differ from the latter only in respect of their origin. The γ -rays affect photographic plates and are capable of ionising gases though the effect is small. With an intense beam of γ -rays, phosphorescence on a fluorescent screen has also been observed.

C. THE ATOM

V.7. Scattering of α -particles : Rutherford's atom. The presence of free electrons was observed during discharge in gases and it was also established at that time that metals on being heated give off electrons. These proved that electrons were present in atoms. But an atom as a whole is neutral. Hence there must exist within the atom positive electrical charge. The emission of α -particles from the atoms of radioactive substances pointed to the possibility of existence of positively charged units within.

Meantime an experimental observation of great significance was made. At the instance of Rutherford, Geiger and Marsden studied the scattering of α -particles by passing them through thin metal sheets. A beam of α -rays was allowed to pass through a narrow hole and then to strike a thin metal foil, say a gold leaf. The direction of motion of α -particles after emerging from the metal sheet was traced by allowing them to produce scintillations on a fluorescent screen. It was noticed most of the particles passed straight through the metal or suffer very slight deflection. This suggested that matter consisted largely of emptiness. But a few of these α -particles (about 1 in 8000) changed their direction quite sharply ; in some cases the deflection was more than 90° . Even in a few cases, the α -particle after the encounter moved backwards i.e., reflected back. The number of α -particles which were strongly deflected, was not large, but this number increased with metal foils with heavier atomic weights.

Now how such scattering of α -particles was rendered possible? The α -particles shoot out with a tremendous speed and to alter their direction of motion, a huge acceleration must be imparted to it by the atom of the metal foil. To reverse its path would require enormous force. The impact of α -particles with electrons of the atom would not cause the deflection of the former, for, the mass of an α -particle is more than 7000 times that of an electron. When an α -particle passed close to an electron in the atom the former would impart energy to the electron sufficient to knock it out of the atom. The result would be a free electron and the residual atom with a positive charge (*i.e.*, positive ion). This means, the α -particle would cause ionisation. It explains the great ionising power of the α -rays actually observed when passed through gases.

For a scattering of more than 90° , the α -particle is required to approach a sufficiently heavy mass carrying powerful similar charge. Even assuming that the entire mass of the atom takes part in repelling the α -particle it was shown by a simple calculation from Coulomb's Law that the α -particle must approach the charge within a distance of the order of 10^{-12} cms. To explain the mechanism of the big deflections of the α -particles, it thus becomes necessary to presume the presence of positive charges concentrated within a volume of diameter less than 10^{-12} cms inside the atom. Moreover, practically the entire mass of the atom should also be concentrated within that volume. Only under these conditions, can an α -particle recoil or suffer large deflection (after colliding with a concentrated positive charge and a large mass). An impact of such type would be similar to the rebounding of a rubber ball from a big stone.

From these considerations, Rutherford was led to propose a nuclear theory for the structure of the atom (1911). The theory may be broadly summarised as follows.

(i) The atom consists of a very minute nucleus at its centre in which is concentrated practically the entire mass of the atom. The dimension of the nucleus is negligible compared to the radius of the atom. The radius of an atom is of the order of 10^{-8} cms and that of the nucleus 10^{-13} cms.

(ii) The entire positive charge also resides in the nucleus. The positive charge is Ze , where e is the unit charge equivalent in magnitude to that of an electron and Z is the number of such units of charge existing in the nucleus.

(iii) Outside the nucleus, there are Z electrons, called *extra-nuclear* electrons, so that the atom is ultimately neutral. These electrons move around the nucleus in different orbits constantly as otherwise the electrons would fall on the nucleus. The arrangement is thus quite similar to the Solar system; the nucleus corresponds to the sun and the extra-nuclear electrons are like the revolving planets.

(iv) The number of positive charges (Z) in the nucleus is the *atomic number* of the element and really represents the ordinal number of the position of the element in the periodic table. Z is thus the atomic number and also the number of revolving extra-nuclear electrons of the atom. Atoms of all elements are structurally similar; they differ only in the number of positive charges in the nucleus. The fundamental characteristic of an element is its atomic number Z . The chemical properties of the element are however based on the extra-nuclear electrons and their arrangement.

With this picture of the nuclear atom, Rutherford proceeded to analyse mathematically the α -ray scattering by thin metal foils. When a beam of α -particles is allowed to pass through a metal foil, some particles may pass close to a nucleus while others at a greater distance. The effect is that the α -particles would be deflected differently after traversing a certain thickness of matter. It was therefore necessary to calculate the number of particles scattered at different angles. Rutherford made a statistical investigation of the α -particles scattered at various angles. It must be realised that the scattering will also depend upon the thickness (t) of the metal foil as also its density. The higher the density the greater is the number (n) of atoms (or their nuclei) present in a given volume. An α -particle approaching a nucleus along the path AO towards a nucleus at O may be deflected along OB at an angle θ from the original direction (Fig. V.8). The deflection is due to the repulsive force governed by Coulomb's law between the charge Ze of the nucleus of

the metal atom and $2e$ of the α -particle. From these considerations, Rutherford derived the equation

$$N = N_0 \cdot t \cdot n \left(\frac{Ze^2}{mv^2} \right)^2 \cdot \frac{1}{r^2 \sin^4 \theta/2}$$

where N is the number of α -particles out of total number N_0 scattered over 1 cm at a distance r at an angle θ ; m and v are the mass and speed of the α -particle.

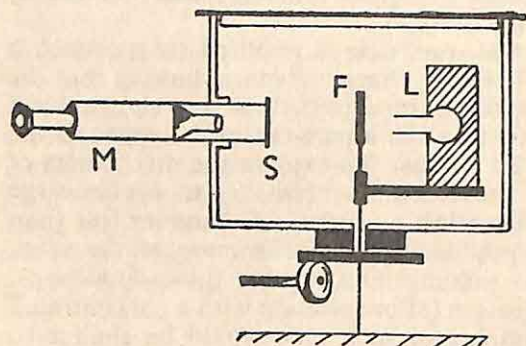


FIG. V.9 Geiger-Marsden apparatus for verification of Rutherford equation

table such that the microscope with the screen S may be fixed at different angles with respect to a fixed position of the source L and metal foil F . Air is pumped out of the instrument and the flashes on the fluorescent screen were counted at different position of the screen and microscope. Thus, it was possible to obtain the number of particles (N) scattered at different values of θ .

The Rutherford equation could not be verified at the time straightway, for a direct determination of the atomic number Z was not then possible. Yet the validity of the equation was established in other ways.

(i) It was shown that $N \times \sin^4 \theta/2$ was a constant for different values of θ , which was a requirement of the equation.

(ii) Using scattering foils of different thickness (t) it was observed that the number of scattered particles (N) at a given angle was directly proportional to t .

(iii) In another set of experiments, the velocity of the incident α -particles was changed by placing thin sheets of mica between the source and the scattering metal foil F . The velocity was calculated from the relation R (range = av_0^3). It was seen that Nv^4 was a constant when v was varied. This again was expected from the equation since $N \propto 1/\epsilon^2$, at angle θ where ϵ = energy of the particles.

The essential correctness of the Rutherford's nuclear theory was thus established. A direct determination of the nuclear charge Ze was possible sometime

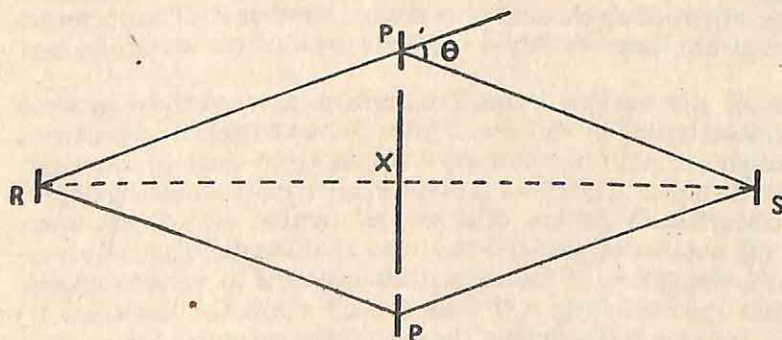


FIG. V.10 Chadwick's arrangement for determination of Ze

An experimental verification of this equation, called the Rutherford equation, convinced the correctness of the nuclear concept. Geiger and Marsden determined the number of α -particles scattered at various angles with the help of an arrangement shown in Fig (V.9).

A narrow beam of α -particles was allowed to come out from a groove in a lead block L and impinge on a thin metal foil F . After scattering, the particles struck a screen S ; the scintillations so produced were observed by the microscope M . The whole system was mounted on a turn-

table such that the microscope with the screen S may be fixed at different angles with respect to a fixed position of the source L and metal foil F . Air is pumped out of the instrument and the flashes on the fluorescent screen were counted at different position of the screen and microscope. Thus, it was possible to obtain the number of particles (N) scattered at different values of θ .

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later through the work of Chadwick (1920). α -particles from a source R (Fig. V.10) were allowed to be scattered by a thin metal foil PP' which was taken in the form of an annular ring. The scattered particles after deflection at an angle θ were

counted from scintillations on a small screen S of known area placed on the axis of the cone RPP' , in which RP is equal to SP . The total number of particles striking PP' was known by counting the number reaching S directly from R .

When scattered rays were studied, the direct rays from R were cut off by a thick plate X. Knowing other constants, Ze was directly obtained from the Rutherford equation.

The results of Chadwick's experiments for some of the metals are given here.

Element	Cu	Ag	Pt
Nuclear charge	29.3e	46.3e	77.4e
Atomic number	29	47	78

V.8. Moseley's Experiment : Atomic Number Determination. It had been known for sometime that when an element present in the anticathode was bombarded with cathode ray electrons the X-rays emitted were characteristic of the elements. In 1913, the young English physicist Moseley investigated systematically the spectra of the X-rays emitted by different elements. He used anticathodes made of the element to be studied or coated them with one of its compounds. The X-rays emitted from these anticathodes were diffracted through a crystal of potassium ferrocyanide and the resulting rays were allowed to fall on a photographic plate. From the relative positions in the photograph, the frequencies of the lines were determined.

The outstanding feature of the X-ray spectra was their simplicity and their great similarity to each other. In Fig (V.11) are shown the lines in the X-ray spectra of some neighbouring elements of the periodic table from potassium to zinc.

The characteristic spectrum of each element was found to consist of two lines, one being very prominent called the K_α -line. (In reality each of these two lines was a doublet closely spaced, i.e., there were four lines). A glance at this picture would reveal that the characteristic frequency of a line,

say K_α -line, changed regularly, from element to element, i.e., with the ordinal number of the element in the periodic table. To pass from the spectrum of one element to that of the next, it was only necessary to shift the frequency to the left by a definite amount. In other words, there was a simple relation between frequency of the line and the position in the periodic table.

These lines were called the lines of the K-series. But when elements of comparatively heavier atomic weights (beyond Neon) were taken, besides the K-series lines, another set of lines were obtained on diffraction called the L-series lines. With still heavier atoms, three sets K-, L- and M-series lines were obtained.

By comparing the frequency (ν) of the most prominent line in the spectrum of a series, Moseley established a relation between the ordinal number (Z) of the element in the periodic table and the frequency ν which was given by the expression

$$\nu = a(Z-b)^2$$

where a and b are constants. But magnitudes of a and b were different for K-, L- and M-series. For the lines of the K-series, $a = 2.47 \times 10^{15}$ and $b = 1$. The relation may also be expressed in the form,

$$\nu^{\frac{1}{2}} = Z.a^{\frac{1}{2}} - b.a^{\frac{1}{2}}$$

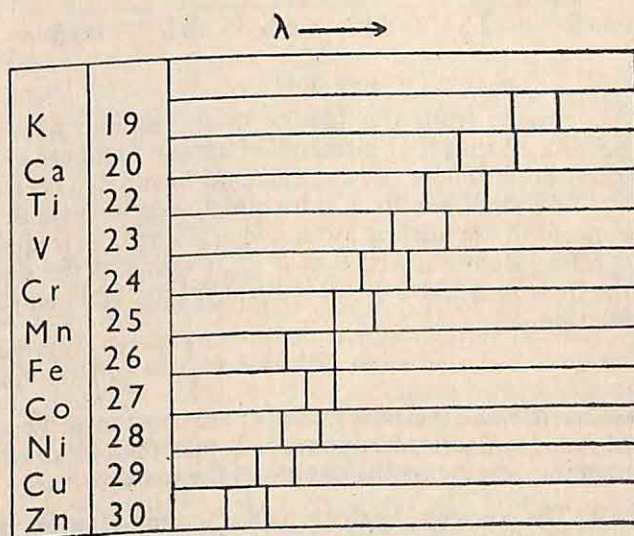


FIG. V.11 X-ray spectra (K-series)

which predicts linearity between Z and $\sqrt{\nu}$. This was realised, as shown in Fig. (V.12).

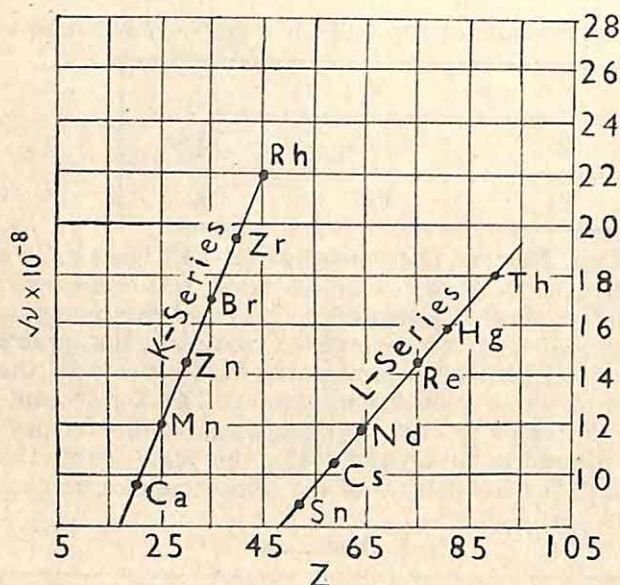


FIG. V.12

Again, from the blanks in the atomic number-frequency curves Moseley postulated that four elements of atomic numbers 43, 61, 72 and 75 remained to be discovered. These missing elements have since been discovered.

We shall see in a subsequent section how Bohr developed the Rutherford concept of the nuclear atom and explained the frequencies of the lines in the atomic spectra. Bohr showed that if Z' is taken as the nuclear charge, the frequency of the lines in a series of the optical spectra (Lyman series) may be expressed by the relation,

$$\nu = Rc(Z'-1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} Rc.(Z'-1)^2$$

where R and c (velocity of light) are constants. This relation is the same as that of Moseley's K -series frequencies. It may then be concluded that $Z = Z'$, i.e., atomic number, represents the charge in the nucleus.

V.9. The Nucleus. Hydrogen has the simplest atom with only one electron revolving around its nucleus. The nucleus of a hydrogen atom therefore carries a unit positive charge. When the electron of this atom is removed, the bare nucleus with a unit charge and a mass practically the same as that of the hydrogen atom (since mass of the electron is negligible) is left and is called a *proton*. The proton is a fundamental particle of unit mass (in atomic wt. units) with a unit positive charge. The positive charge of the nucleus of atoms of other elements consists of two or more protons. Helium (at. no. 2) has two units of positive charge in its nucleus. That is, there are two protons in its nucleus. Similarly, an atom of sodium (at. no. 11) has 11 protons in its nucleus.

We have seen that the entire mass of the atom is concentrated in the nucleus, the weight of the extra-nuclear electrons being negligible. But except in the case of hydrogen, the protons alone cannot account for the total mass of the same. For example; helium atom is 4 times as heavy as an atom of hydrogen, hence helium nucleus must be 4 times heavier than a proton. But, helium nucleus contains 2 protons, which accounts for two units of mass. The other two units must have been due to other particles. Similarly, oxygen (at. no. 8) has 8 protons in its nucleus. But the atomic wt. of oxygen is 16, which means that its nucleus is 16 times heavier than a proton. The other 8 units of mass must have been then contributed by other particles. These facts lead to the inevitable conclusion that in the nucleus are also present other heavy particles having no electrical charge.

That the ordinal number, i.e., the atomic number (Z), is the fundamental characteristic of the element was obvious. Moseley's work immediately cleared two difficulties of the periodic table. There were instances where elements with higher atomic weight had to be placed earlier than the elements with lesser atomic weight, e.g., Argon and Potassium, Tellurium and Iodine, etc. Such anomaly was removed when Moseley showed that atomic number of iodine was greater than that of tellurium though the atomic weights were not so. The same was the case with other anomalous pairs.

We now know there are present in the nucleus electrically neutral particles having almost the same mass as that of the proton. These are *neutrons*. Though the existence of the neutron was predicted much earlier, its discovery was made by Chadwick only in 1932.

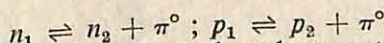
In 1930 Bothe and Becker observed that if boron and beryllium be bombarded with α -particles, a highly penetrating radiation was emitted. Since it was not deflected in a magnetic field, the radiation was regarded as a form of γ -rays. Soon after, Curie-Joliot showed that when hydrogen-containing compounds, such as hydrocarbons, were bombarded with this radiation, protons were emitted. Since hydrogen nucleus contains a proton only, the phenomenon could not be a case of disintegration. The proton is ejected from a collision with this radiation. In 1932, Chadwick made a thorough investigation of the number and range of the ejected protons and concluded that the neutral radiation emitted from beryllium could not be γ -rays. The radiation consists of uncharged particles having mass almost equal to that of a proton. Since then much work has been done and it is now established that the mass of the neutron is 1.00898 (when O = 16.00).

The atomic nucleus therefore contains two kinds of particles—neutrons and protons*. Only the simplest nucleus, namely that of hydrogen, has no neutron. The number of protons represents the charge and hence the atomic number of the element. The total number of protons and neutrons together represent the mass of the atom. Thus, in carbon (at. no. 6, and at. wt. 12), there are 6 protons and 6 neutrons in its nucleus. In chlorine (at. no. 17, at. wt. 35.5), 17 protons and 18 neutrons constitute the nucleus.

The size of the nucleus is indeed very small, its diameter is of the order of 10^{-13} cms. In such a small compass, all the protons and neutrons are clustered together. What holds the nucleus together? Normally the protons should repel one another because of their charge. There must then be some other force which overcomes the coulombian repulsion and provides stability. To explain this, Yukawa in 1935, proposed a theory which is now believed to be correct. The particles—neutrons and protons—are held together by what is termed as 'exchange force'. These forces are extremely short-range and in close proximities they outweigh the long-range electrostatic repulsion. So that when the dimension is of the order of 10^{-13} cms the attraction between proton—proton, neutron—proton or neutron—neutron is practically the same. In virtue of the exchange force there is a constant interchange, within the nucleus, between neutron—proton, proton—neutron or even between two protons or two neutrons. In fact, the particles, neutrons and protons, are regarded as the two different states of the same fundamental particle, now called nucleon. Yukawa further showed mathematically that such exchanges between neutron and proton would be possible only through a small intermediate particle, which was named a meson. That means two nucleons are held together through the sharing of a meson. The mesons are subatomic particles and are of different types; e.g., μ -mesons (or muons) or π -mesons (or pions). These have extremely short lives and possess a mass of 200~300 times that of an electron. Thus, a proton would release a positive π -meson and would become a neutron, whereas a neutron would release a negative π -meson and become a proton or vice-versa, as indicated below.



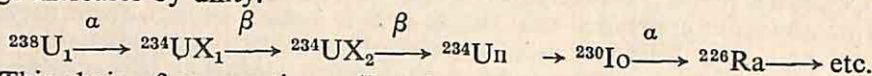
There may also be an exchange of uncharged meson (π^0) between two protons or two neutrons, such as



The theory has its maximum support from the subsequent discovery of mesons from cosmic rays with similar mass and exhibiting the same properties. [See Sec. XVIII.1]

*At one time it was believed that in the nucleus are present protons and electrons. There was always an excess of protons to give the nucleus a positive residual charge. An atom of atomic wt. A was supposed to have A protons in the nucleus along with X electrons, such that $A - X = Z$, Z is the atomic number of the element. The number of electrons outside the nucleus is also Z . The acceptance of this view led to some improbable deductions, for which the theory had to be rejected, especially when the neutron was identified.

V.10. Isotopes. The first radioactive element discovered is uranium. It is an element of the 6th group of the periodic table with the atomic number 92 and atomic mass 238. It emits spontaneously an α -particle to be transformed into Uranium- X_1 (i.e., UX_1). The daughter UX_1 will have an atomic mass 4 units less and charge 2 units less than those of uranium (i.e., at. wt. = 234, at. no. = 90). UX_1 is also radioactive and emits a β -particle to produce UX_2 . Due to loss of a β -particle the nuclear charge will increase by unity, the mass remaining the same. UX_2 in its turn is transformed into U_{II} by ejecting a β -particle and so the process continues until finally the non-radioactive lead is formed. At each stage either an α - or a β -particle is emitted. When an α -particle goes out, the mass decreases by 4 and charge by 2 units; when a β -particle is ejected the mass remains unaltered but charge increases by unity.



This chain of consecutive radioactive transformation from uranium to lead, commonly called the Radioactive series of Uranium, is described below indicating also the variations in mass and charge (i.e., atomic number) of the nucleus. Radium is but a product in this chain being derived from Ionium (Io) and being disintegrated to Radon (Rn).

TABLE : RADIOACTIVE SERIES OF URANIUM

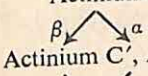
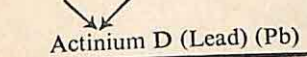
Name and Symbol	Particle emitted	Atomic mass	Atomic number	Half life
Uranium I, (U)	α	238	92	4.6×10^9 years
Uranium X_1 , (UX_1)	β	234	90	24.1 days
Uranium X_2 , (UX_2)	β	234	91	1.14 min.
Uranium II, (U_{II})	α	234	92	2.7×10^5 years
Ionium, (Io)	α	230	90	8.3×10^4 years
Radium, (Ra)	α	226	88	1590 years
Radon, (Rn)	α	222	86	3.8 days
Radium A, (RaA)	α	218	84	3.0 min.
Radium B, (RaB)	β	214	82	26.8 min.
Radium C, (RaC)	β, α	214	83	19.7 min.
$\beta \swarrow$ Radium C' Radium C'' $\alpha \swarrow \searrow \beta$	α, β	214, 210	84, 81	10^{-4} sec./1.3 min.
Radium D, (RaD)	β	210	82	22 years
Radium E, (RaE)	β	210	83	5 days
Radium F, (RaF)	α	210	84	140 days
Radium G, (RaG) (Pb)	$\times$	206	82	Stable

Two other radioactive series met with in nature start with Thorium and Protoactinium. These series are also given here.

TABLE : RADIOACTIVE SERIES OF THORIUM

Name and Symbol	Particle emitted	Atomic mass	Atomic number	Half life
Thorium, (Th)	α	232	90	1.4×10^{10} years
Mesothorium, (MsTh)	β	228	88	6.7 years
Mesothorium, (MsThII)	β	228	89	6.13 hours
Radiothorium, (RaTh)	α	228	90	1.9 years
Thorium X, (ThX)	α	224	88	3.65 days
Thoron (Tn)	α	220	86	55 sec
Thorium A, (ThA)	α	216	84	0.16 sec
Thorium B, (ThB)	β	212	82	10.6 hours
Thorium C, (ThC)	β, α	212	83	1 hour
$\beta \swarrow$ Thorium C' Thorium C'' $\alpha \swarrow \searrow \beta$	α, β	212, 208	84, 81	3×10^{-7} sec./3 min.
(Thorium D) Lead, (Pb)	$\times$	208	82	Stable

TABLE : RADIOACTIVE SERIES OF ACTINIUM

Name and Symbol	Particle emitted	Atomic mass	Atomic number	Half life
Protoactinium, (Pa)	α	231	91	3.2×10^4 years
Actinium, (Ac)	β	227	89	13.5 years
Radioactinium, (RaAc)	α	227	90	19 days
Actinium, X, (AcX)	α	223	88	11.2 days
Actinon, (An)	α	219	86	3.9 sec.
Actinium A, (AcA)	α	215	84	1.8×10^{-3} sec
Actinium B, (AcB)	β	211	82	36 min
Actinium C, (AcC)	β, α	211	83	2.16 min
 Actinium C', Actinium C''	α, β	(211, 207)	84, 81	5×10^{-3} sec./4.7 min
 Actinium D (Lead) (Pb)	$\times$	207	82	Stable

The entity of an element is solely determined by the nuclear charge, *i.e.*, the atomic number. In other words, the properties of an element are fundamentally based on the atomic number. A glance at the radioactive series will reveal that there are radioactive elements, genetically connected, which have the same atomic number but with different atomic masses. Since the atomic number is the same, there shall be identity of properties. U_I and U_{II} will bear this out. Both have atomic number 92, but their atomic weights are 238 and 234, and these two have different radioactivity. Many other such examples may be easily found. Now, the atomic number is the ordinal number of the position of an element in the periodic table. Both U_I and U_{II} therefore should be given the same place in the periodic table. Their identical properties also demand the same. Such groups of elements which differ in atomic masses but have the same atomic number have been given the name 'isotopes' by Soddy.

Experimental evidence indicating the existence of isotopic elements had already accumulated even before such a possibility could be realised from the study of radioactive series. A very careful estimation of the atomic weight of lead obtained from different sources showed a considerable variation. Lead obtained from thorite was found to have an atomic weight of 207.69 while that from uranium-containing ore was 206.08. This is also the expectation from the disintegration of the radioactive series cited above. Atomic weight of lead from non-radioactive source is 207.2.

When Ionium, parent of Radium, was discovered by Boltwood (1906), he found that its properties were identical with those of thorium. When their salts were mixed, attempts to separate them failed. Moreover, the spectra of the two elements were identical (*i.e.*, atomic number is same). And yet their atomic masses were different. Many other instances of complete identity of properties and their inseparability were noticed, *e.g.*, Radium-D, Thorium-D and Lead; Uranium -I and Uranium-II; Radioactinium and Thorium, Radium and Mesothorium I, etc. The three gaseous emanations had also been found to have identical properties analogous to inert gases.

It is easily understood that in isotopic elements the number of protons must be the same as the atomic number is the same. Since the atomic mass is different, the number of the constituent neutrons must vary. Thus, in the different varieties of lead, the number of protons is always 82 but number of neutrons are 122, 124, 125, and 126. In other words, the association of different number of neutrons with a definite number of protons gives rise to isotopes.

Though the isotopes were first detected with radioactive elements, most other non-radioactive elements have been shown to have isotopes. Attempt to confirm different mass in the atoms of the same element experimentally began with the investigations of Thomson and met with extra-ordinary success.

V.11. Positive Ray Analysis. Thomson was studying the effect of magnetic and electric fields on the positive rays or canal rays coming out through the perforated

cathode of the cathode ray tube. These beams consist of positively charged particles and are deflected from their normal straight line path by electric or magnetic fields.

Suppose such a beam strikes this paper from above vertically and it is subjected to an electric field X and also a magnetic field H acting simultaneously. The fields are so applied that a particle normally striking at O will be shifted to the right at X due to electric field and towards the top to the position at Y due to the magnetic field (Fig. V.13).

$$OX = k_1 \frac{Xe}{mv^2}; OY = k_2 \frac{He}{mv}$$

where e = charge associated with the particle of mass m having a velocity v . The resulting position of the particle will be at P .

Evidently,
$$\frac{OY^2}{OX} = k \cdot \frac{H^2}{X} \cdot \frac{e}{m}$$

If we have a number of particles with different velocities but with the same e/m ratio and if these are subjected to the given electric and magnetic fields,

$$\frac{OY^2}{OX} = \text{constant}$$

which is the equation of a parabola. Since v is different, OX and OY would be different indicating different positions for P . P will thus describe a parabola as shown in the figure.

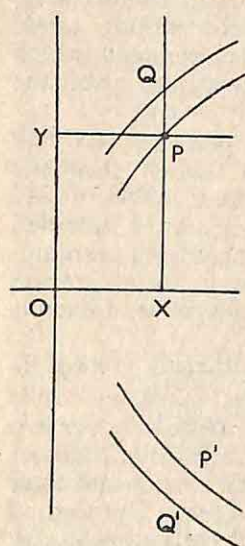


Fig. V.13 Positive ray analysis

If a beam of particles with a different e/m ratio come into the same fields, they would also form a parabola Q , but different from the previous one. For,

$$\frac{OY^2}{OX} = k \cdot \frac{H^2}{X} \cdot \frac{e}{m_1} \text{ and } \frac{OY^2}{OX} = k \cdot \frac{H^2}{X} \cdot \frac{e}{m_2}$$

assuming that charges carried by the two sets be the same. It is easily seen that if different parabolas are experimentally realised by applying same fields, there must be particles having different e/m ratios. The relative values of the masses of the particles can also be estimated from the curves.

A diagrammatic sketch of the apparatus used by Thomson is given in Fig. V.14. He used a long cathode C having a very fine hole at its axis in a discharge tube subjected to about 20000 volts with a vacuum of the order of 0.001 mm of Hg. The fine beam of positive rays emerging out of the narrow aperture into the space S was immediately subjected to simultaneous strong magnetic and electrostatic fields H and X working in parallel. After traversing the space S , they were allowed to strike a photographic plate P , where the expected parabolic streaks were obtained. By reversing the direction of the magnetic field, parabolas were also traced in the other quadrant (P' and Q' , Fig. V.13). Using hydrogen in the discharge tube, a parabola was obtained having e/m value equal to 10^4 emu per gm. This standard to measure the relative masses of the particles producing other parabolas. The parabolas obtained were quite sharp and quite distinct from one another which was the first experimental evidence that atoms had discrete masses.

While experimenting with Neon of atomic weight 20.18, Thomson obtained an intense parabola at the position expected of mass 20; another relatively faint parabola was also detected by him at a position which would correspond to mass 22. By a careful examination avoiding all other possibilities of error, Thomson

concluded that Neon had particles of two different masses of 20 and 22. This indeed was the first confirmation of the existence of isotope in a non-radioactive element. Aston tried to separate the two isotopes of neon and carried out conti-

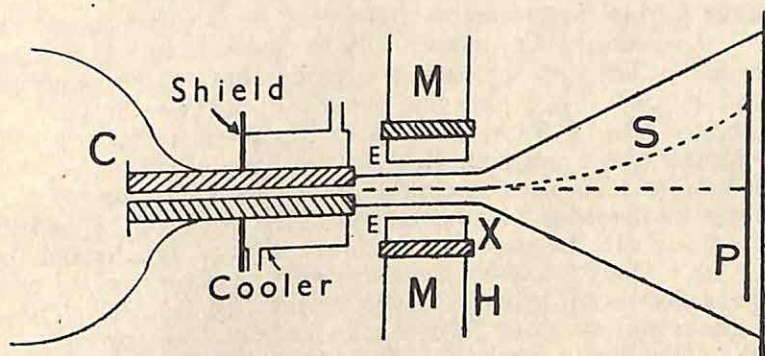


FIG. V.14 Thomson's positive ray apparatus

nuous fractional diffusion of neon through clay-pipe tubes. After innumerable times of repetition, at last he obtained two samples of neon having mol. wts., established by density methods, of 20.15 and 20.28. This confirmed the truth of the two positive ray parabolas for neon isotopes. The two forms had the same spectra and behaved identically otherwise.

Aston's Mass Spectrograph. Considerable improvement on Thomson's parabola technique was made by Aston (1919) with an arrangement since named Aston's Mass Spectrograph. A narrow beam of positive rays emerging out of a pierced cathode was rendered into an extremely fine ribbon by passing through co-axial slits (s_1 and s_2) of approximately 0.02 mm diameter. This fine beam then entered into an electric field maintained by two capacitor plates P_1 and P_2 and was deflected (Fig. V.15). The different particles, even with same mass, were deflected differently as the velocities differed, i.e., the beam spread out. A portion of this spread out rays then passed through a small opening of a diaphragm D and were subjected to a magnetic field H in such a way that the particles were deflected in the same plane but in an opposite direction. The result was that the spread out rays would tend to converge. In fact, by proper adjustment of the apparatus and careful manipulation of the applied fields, it was possible to converge the rays (having particles of the same mass) at a point P on a photographic plate, where a sharp line was obtained. For particles with a different mass, a separate line would be formed. In fact, there would be distinct lines on the photographic plate for each kind of particles, like the lines of an optical spectra. Hence, this was termed mass spectrograph. In fact, different lines were formed on the plate P .

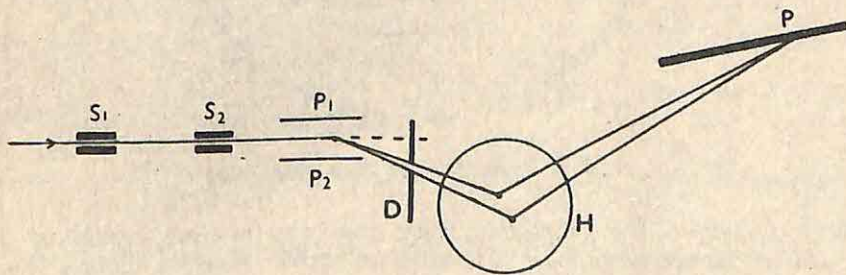


FIG. V.15 Principle of Aston's Mass spectrograph

The mass of the particle corresponding to a line was evaluated by comparing with a line produced by particles of known mass, say $O^+ = 16$, or $C^+ = 12$.

With the mass spectrograph, it was not only possible to detect the isotopes of an element and their relative abundance in a sample, but also the masses of the isotopes with an accuracy of one in ten thousand*. Later more refined and different mass-measuring techniques were developed in the hands of Dempster, Bainbridge, Nier etc. We may describe here the Bainbridge technique.

Bainbridge's Mass Spectrograph. His technique is based on the fact that if a beam of ions all having the same velocity be subjected to a magnetic field, the particles would deflect and separate into groups having the same e/m values. A fine pencil of positive rays emerging out of two narrow slits (s_1 and s_2) is led into a velocity-selector S , which consists of two parallel plates P_1 , P_2 between which an electric and a magnetic field are applied. The fields are so adjusted that the deflections take place in opposite direction. Only those particles which are undeviated by the fields would come out of the exit L of the velocity selector (Fig. V.16). These are the particles which are affected equally but in opposite directions. The velocity (v) of all these emerging particles is given by $v = X/H$ where X is the electric and H is the magnetic field. (see Sec. V-3). These particles then enter into a uniform powerful magnetic field O (15000 gauss), so that these are deflected fully into a semicircle. The radius of this curvature is given by

$r = \frac{mv}{eH_0}$ where H_0 is the magnetic field. Since v , H_0 and e (assuming equal charge) are constant, the radius will be directly proportional to m , mass of the particle. That is, the particles of different m will be deflected through different semicircles. Each group of particles of a definite mass strikes the plane KK' through L and focus at a point forming a line on a photographic plate placed there. The distances LK , LK' are thus measures of the mass of the particles of different groups. The series of lines indicate the existence of isotopes and their masses can be accurately evaluated also.

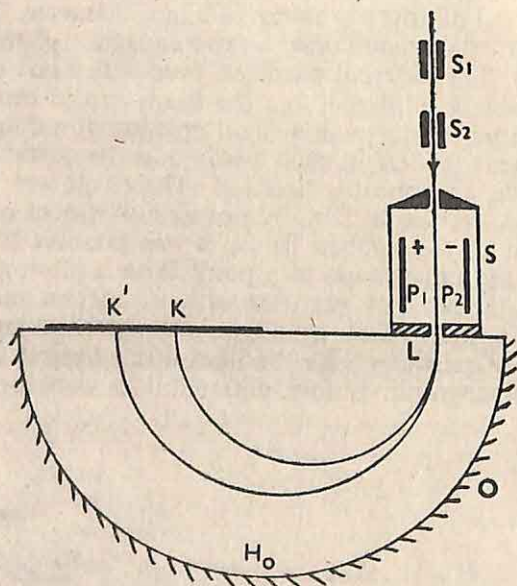


FIG. V.16 Bainbridges' mass spectrograph

With the help of these methods, it has now been possible to establish definitely that most of the elements have a number of stable isotopes. Only a few such as

*For an approximate calculation, see Tolansky : Introduction to atomic physics, chapter IV.

Ref : Aston : Mass spectra and isotopes, 1942.

Be, Al, Au, Bi etc. have no isotopes. In the table below are listed the non-radioactive elements with their isotopes.

TABLE : THE ISOTOPES OF NON-RADIOACTIVE ELEMENTS

<i>Element</i>	<i>At. No.</i>	<i>Isotopes</i>	<i>Element</i>	<i>At. No.</i>	<i>Isotopes</i>
H	1	1, 2	Cd	48	106, 108, 110, 111, 112, 113, 114, 116
He	2	3, 4	In	49	113, 115
Li	3	6, 7	Sn	50	112, 114, 115, 116, 117, 118, 119, 120, 122, 124
Be	4	9	Sb	51	121, 123
B	5	10, 11	Te	52	120, 122, 123, 124, 125, 126, 128, 130
C	6	12, 13	I	53	127
N	7	14, 15	Xe	54	124, 126, 128, 129, 130, 131, 132, 134, 136
O	8	16, 17, 18	Cs	55	133
F	9	19	Ba	56	130, 132, 134, 135, 136, 137, 138
Ne	10	20, 21, 22	La	57	139
Na	11	23	Ce	58	136, 138, 140, 142
Mg	12	24, 25, 26	Pr	59	141
Al	13	27	Nd	60	142, 143, 144, 145, 146, 148, 150
Si	14	28, 29, 30	Pm	61	147
P	15	31	Sm	62	144, 147, 148*, 149, 152, 154
S	16	32, 33, 34, 36	Eu	63	151, 153
Cl	17	35, 37	Gd	64	152, 154, 155, 156, 157, 158, 160
A	18	36, 38, 40	Tb	65	159
K	19	39, 40*, 41	Dy	66	158, 160, 161, 162, 163, 164
Ca	20	40, 42, 43, 46, 48	Ho	67	165
Sc	21	45	Er	68	162, 164, 166, 167, 168, 170
Ti	22	46, 47, 48, 49, 50	Tm	69	169
V	23	51	Yb	70	168, 170, 171, 172, 173, 174, 176
Cr	24	50, 52, 53, 54	Lu	71	175, 176*
Mn	25	55	Hf	72	(172), 174, 176, 177, 178, 179, 180
Fe	26	54, 56, 57, 58	Ta	73	181
Co	27	57, 59	W	74	180, 182, 183, 184, 186
Ni	28	58, 60, 61, 62, 64	Re	75	185, 187*
Cu	29	63, 65	Os	76	184, 186, 187, 188, 189, 190, 192
Zn	30	64, 66, 67, 68, 70	Ir	77	191, 193
Ga	31	69, 71	Pt	78	192, 194, 195, 196, 198
Ge	32	70, 72, 73, 74, 76	Au	79	197
As	33	75	Hg	80	196, 198, 199, 200, 201, 202, 204
Se	34	74, 76, 77, 78, 80, 82	Tl	81	203, 205
Br	35	79, 81	Pb	82	204, 206, 207, 208
Kr	36	78, 80, 82, 83, 84, 86	Bi	83	209
Rb	37	85, 87*			
Sr	38	84, 86, 87, 88			
Y	39	89			
Zr	40	90, 91, 92, 94, 96			
Nb	41	93			
Mo	42	92, 94, 95, 96, 97, 98, 100			
Tc	43	99			
Ru	44	96, (98), 99, 100, 101, 102, 104			
Rh	45	101, 103			
Pd	46	102, 104, 105, 106, 108, 110			
Ag	47	107, 109			

*These have weak radioactivity with long half-lives.

V.12. Separation of Isotopes. Because of their identical chemical properties, separation of isotopes by chemical methods generally failed. Isotopes have however been separated by application of physical methods ; some of these are mentioned here.

(a) *Electromagnetic Separation.* Positive rays containing the isotopes were first accelerated in an electric field and then led into a powerful magnetic field, which causes a deflection of the beam. The particles of the positive beam however form groups of different masses which spread out at different angles under the magnetic field as in Bainbridge method. These different groups are collected in separate receptacles. The electromagnetic procedure proved to be an efficient one and was successfully employed in separation of both light and heavy isotopes. The outstanding case is its application in the large scale separation of ^{235}U and ^{238}U .

(b) *Diffusion Method.* Through a porous barrier a gas diffuses at a rate which is inversely proportional to the square root of its molecular weight. The mixture of isotopes (or their compounds) in the gaseous form are allowed to diffuse through a clay-pipe tube when the diffused gas is enriched in the lighter material. The separation factor (s) of a process is the ratio of concentration of two species after processing to that before processing, i.e.,

$$s = \frac{c'_1/c_1}{c'_2/c_2},$$

where (c_1, c_2) and (c'_1, c'_2) are concentrations before and after processing. For a single stage of diffusion, by Graham's Law,

$$s = (m_2/m_1)^{\frac{1}{2}}$$

where m_2 and m_1 are the mol. wts. of the two species.

Aston, we have mentioned earlier, made the first attempt to separate Neon isotopes by this process and succeeded in concentrating ^{22}Ne to some extent. Neon normally contains 90% ^{20}Ne and 10% ^{22}Ne . A single barrier will enrich a constituent isotope of neon to the extent of $\sqrt{22/20} = 1.049$ which indeed is very small. This explains the necessity of continuous successive diffusions, often several hundred times. In 1932, Hertz employed a cascade of 48 diffusion pumps in series in a closed circuit and succeeded in obtaining a sample of neon with the composition 99% ^{20}Ne and 1% ^{22}Ne . The method has been employed in many other cases. By successive diffusions, hydrogen of mass 2 (i.e., heavy hydrogen ^2H) was practically completely separated from the lighter isotope, the normal hydrogen, ^1H .

Separation of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ in which the former is present to an extent of about 0.7%, has also been successful with this method. For a single stage, the separation factor is $s = \sqrt{352/349} = 1.0043$ theoretically. In isolating 99% $^{235}\text{UF}_6$ the factor should be $s = \frac{99/1}{7/1000} = 14100$ times.

It means many thousand diffusions would be necessary, which however have been achieved in atomic plant project.

(c) *Thermal diffusion method.* In 1938, Clausius and Dickel used a 36-metre long vertical pipe with an electrically heated wire running down its axis to separate isotopes. The walls of the pipe were kept very cold. When a mixture of isotopes in gaseous form, is led in, thermal diffusion causes concentration of lighter component near the hot wire and the heavier component near to the cold walls. Moreover, due to thermal convection, the heavier component goes downwards along the cold wall while the lighter component goes up along the hot wire. Thus there are two streams moving in opposite directions having different proportions of a component isotope. With chlorine gas, practically a complete separation was possible with this method. The method has increasing applications now for its evident simplicity and effectiveness.

(d) *Evaporation method.* That the rates of evaporation of isotopic atom (or molecules) from a mixture are inversely proportional to the square roots of their masses has been taken advantage of in separating them. Lighter atoms would leave the surface more easily leaving the residue richer in heavier component. The evaporation has to be carried out at a very low pressure so that the atoms evaporated may not return to the surface. Bronsted and Hevesy and later Honigs-

chmid and Birkenbach, distilling mercury at a low pressure successively obtained fractions differing appreciably in their densities.

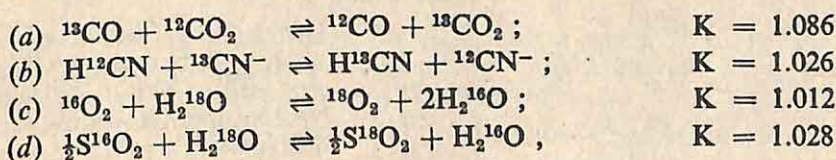
Keesom used this method in separating heavy hydrogen. Ordinary liquid hydrogen, containing 0.02% heavier isotope, was subjected to fractional distillation with an efficient rectification column. In the final sample of the gas, he could obtain about 1.5% of heavy hydrogen.

(e) *Electrolytic method.* Washburn and Urey (1932) found that water in the commercial electrolytic cell which was in use for several years had a higher density and in fact contained a greater proportion of ^2H , heavy hydrogen. During electrolysis of aqueous solution, the lighter isotope of hydrogen ^1H , is preferentially evolved (due to its low overvoltage) and the residual liquid contained a greater proportion of the heavier isotope, ^2H . Starting with 20 litres of water from old electrolytic cells, Lewis and Macdonald electrolysed it until the volume was reduced to 0.5 c.c. This residue was found to have a density of 1.073 containing nearly 70% of heavy water, $^2\text{H}_2\text{O}$. Subsequently this electrolytic method has been employed on a commercial scale to produce almost pure heavy water, so necessary for controlling chain-fission of uranium. This is usually achieved by electrolysis of 0.5 NaOH solution with Ni-electrodes repeatedly.

(f) *Separation by exchange reaction.* Different isotopic species of an element exhibit the same chemical properties but the rates of a chemical process differ somewhat with the different species. In competing reactions, the heavier isotope reacts more slowly. This is particularly noticeable with isotopes of lighter elements. The difference in reactivity has been used in concentrating isotope with the help of *isotopic exchange reaction*. In such a reaction an isotope in one compound exchanges with another isotope of the same element in another compound. If the chemical reactivities of both the isotopes were the same, the equilibrium constant would be unity. But in actual experiments, the equilibrium constant is greater than unity. Urey and Thode concentrated ^{15}N by passing ammonia gas through ammonium nitrate solution trickling down a glass-bead-packed tower when an exchange of the following type took place :



Evidently ^{15}N will increase in proportion in the solution. In fact a concentration of 70% ^{15}N could be obtained in the solution. Similar concentration has also been achieved with isotopes of carbon and oxygen in the processes :



V.13. Deuterium : Heavy Hydrogen. Ordinary hydrogen consists of a mixture of atoms of mass 1 and of mass 2. This has been confirmed by mass spectrographic measurement. The proportion of the heavier atoms in ordinary hydrogen is really small, about 1 in 6500. In the preceding section we have already seen the methods of separation of these two isotopes—particularly with the help of prolonged electrolysis of the liquid from electrolytic cells or by fractional distillation of liquid hydrogen. In the case of heavier elements the relative variation in the mass of isotopic species is quite small, e.g., in lead (206, 207, 208), the variation is within 1% practically. But in the case of hydrogen, the mass of one kind is double that of the other species. Because of this there is some marked difference in the properties of the two isotopes of hydrogen ; and so the heavier variety, commonly called heavy hydrogen, has been given a separate name *deuterium* with the symbol D. The water in which this isotope occurs is called *heavy water*, D_2O . Since the atomic number of the element is 1, the lighter isotope has only one proton in the nucleus, while deuterium nucleus must contain one proton and one neutron. The difference in the properties of hydrogen and deuterium and of water and heavy water is illustrated in the table below.

TABLE

	B. pt. °K	Heat of fusion	Heat of vaporisation	Molar volumes
Hydrogen,	20.38	28 cal	217.7 cal	26.15 c.c.
Deuterium,	23.50	47 cal	303.1 cal	23.17 c.c.

	Density at 20°C	F. pt. °C	B. pt. °C	Surface tension (20°C)	Viscosity × 10 ³ (20°C)	Refractive index (20°C)
Water,	0.9982	0.00	100.00	72.75 dyne/cm	10.01	1.33300
Heavy water	1.1059	3.82	101.42	67.8	12.6	1.32844

V.14. Packing fraction : Mass defect. (a) *Whole number rule.* As long ago as 1815 Prout had suggested that all elements were built up out of hydrogen atoms associated in different numbers. The hypothesis was discarded when many atomic weights were found to be non-integral, such as Cl = 35.4. About a century later when isotopes were discovered the atomic masses were found to be nearly whole numbers. Thus, chlorine was found to be mixture of atoms of masses 35 and 37. Neon (20.2) is a mixture of atoms having mass 20 and mass 22. Even elements whose atomic weight appeared to be integral were found to consist of minute proportion of isotopes. Oxygen (16) is found to be really accompanied with 0.2% of oxygen mass 18 and 0.04% of oxygen mass 17.

On the nuclear theory of the atom, hydrogen atom has one proton and one electron, the mass of the latter is negligible. All other atoms have nuclei made up of protons and neutrons; the weight of a neutron is almost the same as that of a proton. Neglecting the mass of the electrons of the atom, its mass is thus an integral multiple of that of the hydrogen atom. Prout's hypothesis is therefore generally acceptable in a modified form.

(b) *Packing fraction.* With the use of mass spectrograph, very precise determination of atomic masses became possible. Aston found that in most cases there was a slight deviation from whole number for the mass of an isotope. The nearest integral number called the mass number (*A*) is indeed the sum total of the numbers of protons and neutrons. The deviation from the whole number varies from nucleus to nucleus and Aston expressed it in terms of *packing fraction* defined as

$$\text{packing fraction} = \frac{\text{isotope mass} - \text{mass number}}{\text{mass number}} \times 10^4$$

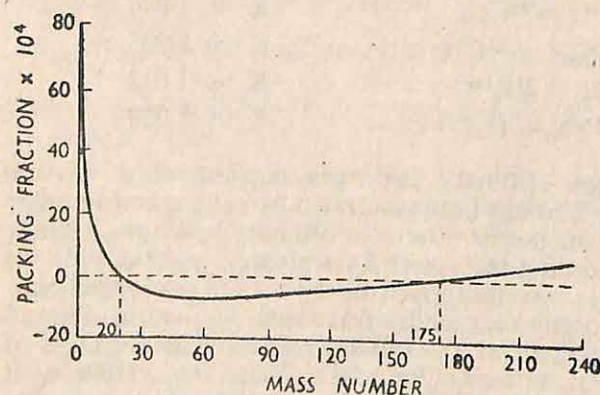


FIG. V.17a

The packing fraction is often negative but sometimes positive also (Fig. V.17a). Negative fraction implies stability of the nucleus while positive fraction indicates instability. Very light and very heavy elements have positive fractions while elements in the middle range have negative packing fraction. The chlorine isotope of mass 35 has the packing fraction—

$$10^4 \times \frac{(34.980 - 35.000)}{35.000} = -5.7$$

(c) *Atomic mass unit.* There had been some difficulty in expressing the atomic masses in view of the uncertainty of the standard. The chemists expressed atomic weight taking naturally occurring oxygen, as the standard, O = 16.000 units. But it is now known that this oxygen is accompanied with two other isotopes, ¹⁷O = 0.04% and ¹⁸O = 0.2%. The atomic weight of ordinary oxygen in this scale would be

$$16.000 \times .9976 + 17.00450 \times 0.0004 + 18.00369 \times 0.002 = 16.0044.$$

The ratio of physicists' to chemists' atomic wt. is thus $16.0044/16.000 = 1.000275$. Since 1961, a unified standard has been accepted for atomic masses where the atomic mass of the carbon isotope ^{12}C has been fixed as 12.0000. In this scale, naturally occurring oxygen has the atomic weight $\text{O} = 15.9999$ and the isotope $^{16}\text{O} = 15.9949$.

An atom of mass number 12 is our standard, hence one atomic mass unit (amu) is given by,

$$1 \text{ amu} = \frac{1}{12} \cdot \frac{12 \text{ gms}}{N_0} \quad (\text{where } N_0 = \text{Avogadro number})$$

$$= \frac{1}{6.025 \times 10^{23}} = 1.66 \times 10^{-24} \text{ gms.}$$

In this scale, the masses of protons and neutrons are

$$\text{proton mass} = 1.008142 \text{ amu} \quad \text{neutron mass} = 1.008983 \text{ amu}$$

(d) *Mass defect.* An atom of mass number (A) and atomic number (Z) has Z protons and $A-Z$ neutrons in its nucleus and Z electrons outside. The mass of the atom is thus expected to be

$$(A-Z)m_n + Zm_p + Zm_e$$

But the isotopic mass (M) is usually found to be less than the theoretically calculated value. The difference is called the mass defect (D);

$$D = (A-Z)m_n + Zm_p + Zm_e - M$$

$$= (A-Z)m_n + Zm - M$$

(where m_n = mass of neutron, m_p = mass of proton, m_e = mass of electron, and mass of hydrogen atom, $m_H = m_p + m_e$)

It is now accepted that the energy required to hold together the constituent particles, protons, neutrons and electrons in the atom is derived from the loss of mass of the particles as measured by the mass defect. The mass lost is rendered into energy in accordance with the Einstein's principle of relativity, $E = mc^2$.

$$\text{One amu is therefore equivalent to } 1.66 \times 10^{-24} (2.997 \times 10^{10})^2$$

$$= 1.492 \times 10^{-3} \text{ ergs.}$$

$$\text{Since } 1 \text{ electron volt (ev)} = 1.6 \times 10^{-12} \text{ ergs, and } 1 \text{ Mev} = 10^6 \text{ (ev).}$$

$$\text{We have } 1 \text{ amu} = \frac{1.492 \times 10^{-3}}{1.6 \times 10^{-12} \times 10^6} = 931 \text{ Mev.}$$

The energy which is derived from the mass lost is responsible for holding the constituent particles together and is hence the binding energy, E . Expressed in Mev units, the binding energy in an atom is given by

$$E_B = 931 \times D = 931 [(A-Z)m_n + Zm_H - M]$$

To illustrate : The mass defect in the deuterium atom (mass, 2.01474 amu) is

$$D = m_p + m_n + m_e - m$$

$$= 1.00814 + 1.00898 + 0.00055 - 2.01474$$

$$= 0.00293$$

$$\text{Hence the binding energy } E_B = 931 \times 0.00293 = 2.72 \text{ Mev}$$

The binding energy of an electron in this case, as we shall see later, is only 14 ev, which is negligible compared to the total binding energy. The average binding energy per particle of the nucleus, i.e., per nucleon, is 1.36 Mev. The mean binding energy per nucleon is different in different atoms. For example,

atom	binding energy (Mev)	mean E_B per nucleon (Mev)
^7Li	39.27	5.61
^{12}C	92.3	7.69
^{20}Ne	160.0	8.00
^{209}Bi	1630.0	7.80

Majority of the nuclei have binding energy lying between 7.5 and 8.5 Mev. In Fig. V.17b, the mean binding energy is plotted against mass number.

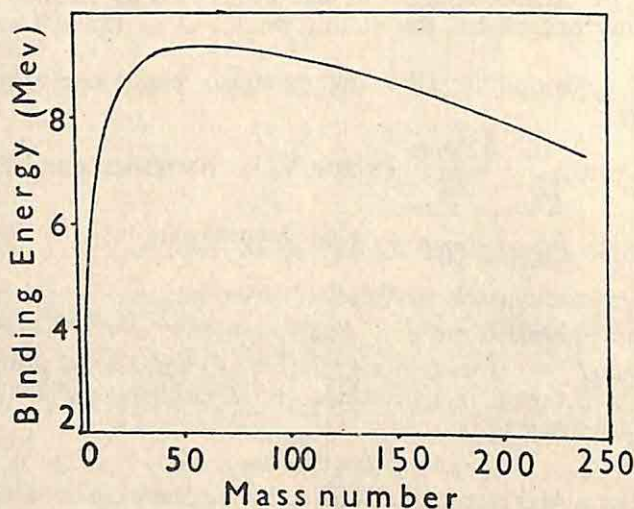


FIG. V.17b Binding energy and mass-number of atoms

The larger the mass defect, the larger would be the binding energy and more stable will be the nucleus.

D. THE QUANTUM THEORY

V.15. Before attempting a further probe into the internal structure of the atom, it is necessary to make a digression in order to be acquainted with the postulates of Planck's Quantum Theory.

Today we are quite familiar with both the wave and the particle properties of light. But up to the close of the last century, light was believed to be undulatory in character; the corpuscular theory was discarded. There were sufficient reasons for it. The simple but most convincing proof was that the wavelengths of the radiations were accurately measured. The phenomena of polarisation and of diffraction and interference produced additional evidence. It was not possible to explain the cancellation of one ray by another (*i.e.*, in interference) without the acceptance of the undulatory nature of light. On the other hand Maxwell, from theoretical considerations, established light to be an electromagnetic radiation and consisted of transverse vibrations produced from a combination of electrostatic and magnetic fields perpendicular to each other.

Towards the close of the nineteenth century, however, an anomalous situation arose and difficulties appeared in explaining the observations in respect of energy distribution of black body radiations. A black-body is one which absorbs completely all the radiations falling upon it and conversely, it emits radiation of all wavelengths. A cavity made with highly insulating wall having a small orifice and heated to a constant high temperature would serve as a black-body. Radiations of all wavelengths would be emitted from the orifice and the same may be treated as black-body radiations. The radiant energy and the same may be analysed by passing through a prism into radiations of various wavelengths. That is, a thermal spectrum of the black-body radiation is obtained and the energy associated with different wavelengths can also be measured. Experiments have revealed that in the case of emission from a black-body, the radiation density is a function of temperature only. The spectral distribution of black-body radiation was studied by Lummer and Pringsheim (1877–1900) experimentally at different temperatures, *i.e.*, the energy E_λ corresponding to each range of wavelength λ was measured. E_λ plotted against wavelength λ produced curves as shown in Fig. V.18. It is easily seen that as the temperature is raised, the average wave-length of the emission becomes shorter.

Attempts were then made to explain the experimental results obtained by Lummer and Pringsheim. In 1893, Wien deduced from purely thermodynamic reasonings that $E_\lambda d\lambda$, i.e., the amount of energy in the spectral region λ and $\lambda + d\lambda$ emitted by a black body at temperature T , is given by (Wien)

$$E_\lambda d\lambda = A \cdot \lambda^{-5} f(\lambda T) d\lambda \dots (a)$$

where A is a constant. This relation was found to be quite satisfactory in the lower range of wavelengths and corresponded with the Lummer-Pringsheim curves but the relation deviated considerably when applied to the longer wavelength region.

Rayleigh and Jeans also derived a relation between E_λ and λ . Assuming stationary waves of all frequencies being emitted from the black body, they first determined the number of possible modes of vibration within the hollow cavity. It was shown from classical mechanics that the number of ways of vibration per unit volume between the frequencies ν and $\nu + d\nu$ is given by

$$dz = \frac{8\pi\nu^2}{c^3} d\nu \dots (b)$$

where c is the velocity of light.

Applying the principle of equipartition of energy for every mode of vibration the average energy is kT . Hence the radiation density is given by

$$E_\nu d\nu = \frac{8\pi\nu^2}{c^3} kT d\nu$$

$$\text{or since } \nu = c/\lambda, \quad E_\lambda d\lambda = 8\pi kT \lambda^{-4} d\lambda \dots (c)$$

This relation was found to hold good with longer waves but failed altogether in the range of short wavelengths. Further the total energy carried by all wave-

lengths, i.e., $\int_0^\infty 8\pi kT \lambda^{-4} d\lambda$ per second will be infinite at all temperatures

except when $T = 0$, which is absurd. Thus the application of classical physics failed to explain the energy distribution in the black body radiations. The correct formula for the energy distribution of black-body radiations was finally discovered by Max Planck.

V.16. Planck's Quantum Theory. In 1901 Planck proposed a revolutionary hypothesis in which he discarded the precept that an oscillator emits or takes up energy continuously and suggested that energy changes must occur in discrete amounts. Planck introduced three assumptions :

- (i) the energy of an oscillator cannot vary continuously but only by discrete amounts. Hence an oscillator has definite energy levels, such as $\epsilon_0, \epsilon_1, \epsilon_2, \epsilon_3, \dots \epsilon_4, \dots$ etc.

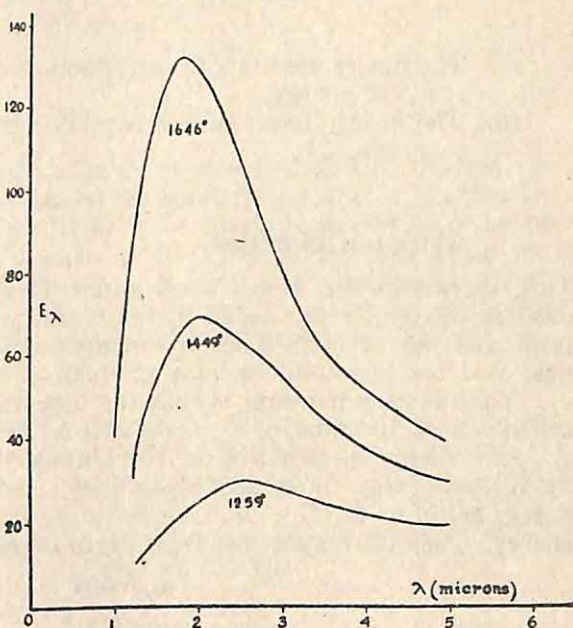


FIG. V.18 Lummer & Pringsheim : Spectral distribution of energy density

- (ii) the oscillator emitting a frequency ν can only radiate in units or *quanta* of the magnitude $h\nu$, where h is a fundamental constant of nature,

$$\epsilon = h\nu$$

This really amounts to introduction of the concept of atomicity in the realm of energy.

- (iii) The energy levels of the oscillator can only be integral multiples of a quantum, *i.e.*,

$$E_n = n\epsilon = nh\nu$$

where n is an integer.

This, known as the Planck's Quantum Theory, profoundly altered the entire outlook of physics. It yielded the most satisfactory theory for black-body radiations and also explained clearly many other phenomena, such as the specific heat of solids, the atomic spectra, photoelectric effect, etc.

The Planck's constant, h , has the dimensions of energy $\times$ time, a quantity called action. Its value, in c. g. s units, is 6.625×10^{-27} erg-sec.

The energy spectrum in the black-body radiation can now be understood in the following way. Imagine a black-body radiator having oscillators with integral energy levels $0, h\nu, 2h\nu, 3h\nu \dots jh\nu \dots$. Let there be n_0 vibrators with zero energy. Then the number of vibrators, in other energy levels, are

$$\begin{aligned} n_1 &= n_0 e^{-h\nu/kT} \\ n_2 &= n_0 e^{-2h\nu/kT} \\ n_3 &= n_0 e^{-3h\nu/kT} \\ n_4 &= n_0 e^{-4h\nu/kT} \\ &\dots \dots \dots \\ n_j &= n_0 e^{-jh\nu/kT} \end{aligned}$$

Hence, the total number of vibrators (N) is given by,

$$\begin{aligned} N &= n_0 + n_1 + n_2 + n_3 + \dots + n_j + \dots \\ &= n_0 + n_0 e^{-h\nu/kT} + n_0 e^{-2h\nu/kT} + n_0 e^{-3h\nu/kT} + \dots + n_0 e^{-jh\nu/kT} + \dots \\ &= n_0 [1 + x + x^2 + \dots], \quad \text{putting } x = e^{-h\nu/kT} \\ &= n_0 \cdot \frac{1}{1-x} \end{aligned}$$

Again the total energy of all the vibrators (E) is given by

$$\begin{aligned} E &= 0.n_0 + h\nu.n_1 + 2h\nu.n_2 + 3h\nu.n_3 + \dots + jh\nu.n_j + \dots \\ &= 0 + h\nu.n_0 e^{-h\nu/kT} + 2h\nu.n_0 e^{-2h\nu/kT} + 3h\nu.n_0 e^{-3h\nu/kT} + \dots + jh\nu.n_0 e^{-jh\nu/kT} + \dots \\ &= n_0 h\nu x. (1 + 2x + 3x^2 + 4x^3 + \dots) \\ &= n_0 h\nu x. \frac{1}{(1-x)^2} \end{aligned}$$

The average energy per oscillator with frequency ν , is

$$\epsilon = \frac{E}{N} = \frac{h\nu x}{1-x} = h\nu \cdot \frac{e^{-h\nu/kT}}{1-e^{-h\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

But we have already seen, that the number of resonating modes between the frequencies ν and $\nu + d\nu$ per unit volume is given by,

$$dz = \frac{8\pi\nu^3}{c^3} d\nu$$

[vide sec. 5-15, eqn. (b)]

Hence the energy density in the region ν and $\nu + d\nu$ will be

$$\left. \begin{aligned} E_\nu d\nu &= \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{e^{h\nu/kT} - 1} d\nu \\ \text{or } E_\lambda d\lambda &= \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda kT} - 1} d\lambda \end{aligned} \right\} \dots (V.1)$$

This relation was found to correspond to the experimental results of Lummer & Pringsheim. The quantum theory thus cleared the anomaly in respect of the black-body radiations. We have also seen (sec III.17) how the problem of specific heats of solids was explained with this theory. In a later section, we shall again see its unique application in the determination of the atomic structure from the interpretation of the line spectra. One of the earliest successes of the quantum theory was in the field of photo-electric phenomenon which we shall briefly mention in the next section.

V.17. Photo-electric Effect. In an evacuated vessel, if suitable light is allowed to fall on a clean metal surface, electrons are emitted from the surface. This phenomenon is called the *photo-electric effect*. Usually a radiation in the ultraviolet region, and also in some cases in the visible region, produces such an effect. The velocity, and hence the kinetic energy, of the emitted electrons was measured by applying an external electric field with a potential V , such that

$$V\epsilon = \frac{1}{2}mv^2$$

where V is the potential required just to stop the photo-electric current.

Experiments have confirmed that the kinetic energy of the photo-electrons is (i) independent of the intensity of illumination of incident radiation and (ii) dependent directly on the frequency of the incident radiation. If, however, the frequency of incident light is decreased, the photo-electric effect disappears at a certain frequency called the "threshold frequency", which is different for different metals. The photo-electric threshold frequency is a very important characteristic of the elements.

The direct dependence of the energy of photo-electron on the frequency of incident radiation cannot be explained by the wave theory. On this theory, light of high intensity (having strong fields) should produce photo-electrons of high velocity and of high kinetic energy. This is not the case; the energy of photo-electron is independent of intensity. On the other hand, sufficiently intense light of low frequency should cause photo-electric emission, which is contrary to experimental results.

In 1905, Einstein explained the photo-electric effect on the basis of Planck's concept of quantum of energy, $\epsilon = h\nu$. Einstein suggested that the emission or absorption of radiant energy takes place in quanta. Each quantum, which is like a particle travelling with the velocity of light, gives up its entire energy to the electron on the surface of a metal. A portion of this energy called the work function (w) is utilised in liberating the electron free from other forces of attraction. The balance of the energy gives the electron its kinetic energy ($\frac{1}{2}mv^2$). Hence we have,

$$h\nu = w + \frac{1}{2}mv^2$$

where ν is the frequency of the incident radiation. This is the *Einstein equation* for photo-electric emission.

Now suppose ν_0 is the threshold frequency, i.e., the frequency just sufficient to drag the electron out, then

$$\begin{aligned} h\nu_0 &= w \\ \therefore h\nu &= h\nu_0 + \frac{1}{2}mv^2 \\ V\epsilon &= \frac{1}{2}mv^2, \text{ we have, } h\nu = h\nu_0 + V\epsilon \end{aligned}$$

Remembering,

$$\text{or } \nu = \nu_0 + \left(\frac{\epsilon}{h} \right) \cdot V$$

This means that if frequency of the incident radiation (ν) be plotted against the applied potential V , a straight line will be obtained whose intercept gives the threshold frequency (ν_0). Moreover the slope of the line will be the same in all cases. This was experimentally confirmed and the value of h calculated from the slope was found to be $h = 6.58 \times 10^{-27}$ erg-sec, which is the same as that obtained from other sources.

This clearly proves the correctness of Einstein's theory of photo-electric emission and incidentally gives a decisive evidence in support of the quantum electric effect. In the table below are given the data for some metals in respect of photo-electric effect.

TABLE

Metal	Threshold frequency ν_0 (Å)	Work function, w (ev)	Ionisation potential (ev)
Na	5000	2.5	5.12
K	5500	2.26	4.32
Cs	6600	1.87	3.88
Cu	2900	4.3	7.69
Ag	2612	4.73	7.54
Zn	3590	3.44	9.37
Fe	2620	4.71	7.83
W	2610	4.73	—
Pt	1962	6.29	—

It will be seen that work function, *i.e.*, the energy required to remove the electron from the surface of a mass is less than the ionisation potential, *i.e.*, the work required to remove an electron from an isolated atom.

Example : Calculate the kinetic energy of a photo-electron emitted from the surface of potassium ($w = 2.26$ ev), when illuminated by radiation 4000 Å .

$$\text{The kinetic energy, } E = h\nu - w = \frac{hc}{\lambda} - w$$

$$= \left[\frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{4000 \times 10^{-8}} - 2.26 \times 1.6 \times 10^{-12} \right]$$

$$= 1.35 \times 10^{-12} \text{ ergs.}$$

E. THE ATOMIC SPECTRA

V.18. The Atomic Spectra. Probably the most important aid in determining the structure of an atom has been the study of radiation emitted and absorbed by the elements. The glowing atoms of an element emit radiations. These radiations, when dispersed through a suitable prism, are found to consist of a large number of lines which are characteristic of the element. The atoms of an element always produce line spectra, often called the *atomic spectra*. The atomic spectra of an element is usually very complex and their analysis is quite a difficult job. The simplest of the atomic spectra, as it is expected, is that of atomic hydrogen. The hydrogen spectrum has been extensively investigated; the frequencies of the lines and the relations between them have also been determined with great precision. This study has helped us to understand the structure of other atoms too.

The hydrogen line spectrum in the visible region consists of four lines (H_α , H_β , H_γ , H_δ) which gradually close up. In fact, these four lines are only a part of a series of lines, nearly thirty in number, extending into the ultraviolet region. As they proceed towards ultraviolet, the lines come closer and closer until these merge. A diagrammatic presentation of the lines is given in Fig. V.19. The position of the lines in the spectra may be indicated in terms of wavelengths (λ) or more generally, in terms of wave number ($\bar{\nu}$), i.e., the number of waves per unit length such that $\bar{\nu} = 1/\lambda$. Thus, the line H_β has $\lambda = 4861.3\text{\AA}$, i.e., $\bar{\nu} = 20572\text{ cm}^{-1}$.

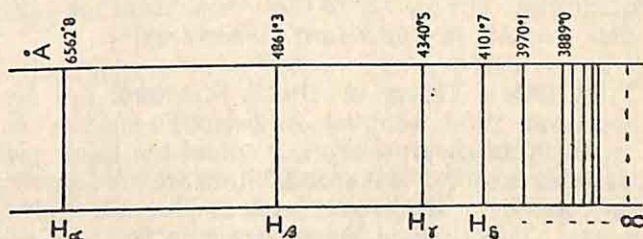


FIG. V.19 Balmer Series

In 1885, Balmer discovered a relation between the wave-number ($\bar{\nu}$) and the position of the lines in the series, since then called the Balmer series. The relation

$$\bar{\nu} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right] \quad \dots (i)$$

where R is a constant called Rydberg constant empirically found to be 109678 cm^{-1} ; and ' n ' is an integer having values of $n = 3, 4, 5, 6$, etc. With this value of R , and putting $n = 3, 4$, etc. it is possible to reproduce the entire Balmer series of lines.

The nature of this relation prompted Balmer & Ritz to realise that there might exist other series of spectral lines in which the first term in eqn. (i) would be different from $\frac{1}{2^2}$. In 1908, Ritz discovered the *principle of combination*, in which it was found that the wave-number of any line in a series would be the difference of two square terms, as

$$\bar{\nu} = R \left[\frac{1}{m^2} - \frac{1}{n^2} \right] \quad \dots (ii)$$

where R is the same Rydberg constant, and m and n are integers, such that $n > m$.

In fact, four other series have later been discovered in the entire spectrum of hydrogen all of which are governed by the relation (ii) mentioned above. In the ultraviolet region, Lyman series was soon found in which $m = 1$ and $n = 2, 3, 4, \dots$

$$\text{Lyman series : } \bar{\nu} = R \left[\frac{1}{1^2} - \frac{1}{n^2} \right] \quad \dots (iii)$$

Similarly in the near and far infra-red regions, three other series of lines have been observed :

$$\left. \begin{array}{l} \text{Paschen series : } \bar{\nu} = R \left[\frac{1}{3^2} - \frac{1}{n^2} \right] ; n = 4, 5, 6, \dots \\ \text{Brackett series : } \bar{\nu} = R \left[\frac{1}{4^2} - \frac{1}{n^2} \right] ; n = 5, 6, 7, \dots \\ \text{Pfund series : } \bar{\nu} = R \left[\frac{1}{5^2} - \frac{1}{n^2} \right] ; n = 6, 7, 8, \dots \end{array} \right\} \quad \dots (iv)$$

A theoretical basis to explain the formation of line spectra and its obedience to the Ritz principle was not obvious. We know that in the hydrogen atom, a single electron revolves in a circle round a proton as nucleus. According to classical mechanics, as the energy is radiated by the electron, the orbital radius must also

change and ultimately the electron should fall into the nucleus. The energy should therefore be radiated in a continuum and the observed line spectra indicating discrete energy changes is not expected. The classical theory therefore cannot explain the formation of line spectra. Not only this, there remains the other question as to why the wave number of these lines are represented as the difference of two quantities. The answer to these came from the young Dane, Niels Bohr, who was then working in Rutherford's laboratory.

V.19. Bohr's Theory of Atomic Structure. For an explanation of the hydrogen spectrum, Bohr adopted Rutherford's nuclear model for the hydrogen atom in which an electron revolves round the single proton at the central nucleus. It was also accepted that spectral lines are produced by atoms one at a time and that for each line a single electron is responsible. Bohr then introduced two new postulates. These postulates appeared to be quite arbitrary at the time they were proposed but subsequently proved to be reasonably valid from wave-mechanical considerations. These two postulates are:

(i) The electron can revolve round the nucleus in only some definite orbits. The permissible orbits are those for which the angular momentum of the electron is an integral multiple of $h/2\pi$. These are termed stationary orbits and no energy is radiated when the electron revolves in a stationary orbit.

The angular momentum, $mvr = nh/2\pi$, where n is an integer called the quantum number indicating the energy level.

(ii) During the emission or absorption of radiant energy, the Planck-Einstein equation, $\epsilon = h\nu$ is obeyed. That is, radiant energy is emitted or absorbed in whole quanta $h\nu$. If E_i and E_f be the initial and final energy levels during emission or absorption of energy, then

$$h\nu = E_i - E_f$$

where ν is the frequency of the radiation. It is obvious radiation will be emitted only when an electron will jump from a stationary orbit of higher energy to one of lower energy.

Now consider an electron moving in the n^{th} orbit at a distance r from the nucleus of charge Ze , Z being the atomic number. We know, its angular momentum

$$mvr = \frac{nh}{2\pi} \quad \dots (i)$$

The electrostatic force on the electron is $\frac{Ze.e}{r^2}$ and the centrifugal force is $\frac{mv^2}{r}$ and

these must balance one another in a stationary orbit. Hence,

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad \dots (ii)$$

$$\text{i.e., the kinetic energy, } E_k = \frac{1}{2}mv^2 = \frac{Ze^2}{2r} \quad \dots (iii)$$

The potential at a distance r from the central charge Ze is given by $\frac{Ze}{r}$.

$$\text{Hence, its potential energy, } E_p = -\frac{Ze^2}{r} \quad \dots (iv)$$

The total energy, therefore, would be

$$E = E_k + E_p = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r} \quad \dots (v)$$

$$\text{For H-atom, } Z = 1, \text{ hence } E = -\frac{e^2}{2r} \quad \dots (vi)$$

By eliminating v from equation (i) & (ii) the radius of the stationary orbit is given by

$$r = \frac{n^2 h^2}{4\pi^2 m e^2 Z} = \frac{n^2 h^2}{4\pi^2 m e^2} \quad (\text{since } Z = 1) \quad \dots (vii)$$

For the permissible stationary orbit nearest to the nucleus, $n = 1$. Hence the radius of the 1st Bohr orbit will be

$$r_1 = \frac{h^2}{4\pi^2 m e^2} = (6.625 \times 10^{-27})^2 / [4 \times (3.14)^2 (4.8 \times 10^{-10})^2 \times 9.11 \times 10^{-28}]$$

$$= 0.529 \text{ \AA}$$

using the standard values of m , e and h , available from other sources. This value is nearly the same as the one obtained from the kinetic theory considerations. The radius of any other orbit of quantum number n will be given by

$$r_n = n^2 \cdot \frac{h^2}{4\pi^2 e^2 m} = n^2 r_1 \quad \dots (viii)$$

From equations (vi) and (vii), the energy of the electron in the n^{th} stationary orbit is

$$E_n = \frac{-2\pi^2 m e^4}{n^2 h^2} \quad \dots (ix)$$

Suppose an electron jumps from the n^{th} level to the n'^{th} level, where $n > n'$. The energy at the n'^{th} level is

$$E_{n'} = \frac{-2\pi^2 m e^4}{n'^2 h^2}$$

The difference of energy is emitted in the form of radiation of, say, frequency, ν .

$$\therefore h\nu = \frac{-2\pi^2 m e^4}{h^2} \left[\frac{1}{n^2} - \frac{1}{n'^2} \right]$$

or

$$\nu = \frac{2\pi^2 m e^4}{h^3} \left[\frac{1}{n'^2} - \frac{1}{n^2} \right]$$

The corresponding wave-number ($\bar{\nu}$) of the radiation shall be

$$\bar{\nu} = \frac{2\pi^2 m e^4}{ch^3} \left[\frac{1}{n'^2} - \frac{1}{n^2} \right] \quad \dots (x)$$

The empirical relation derived from Balmer series lines, and also from Lyman and other series for the wave number is

$$\bar{\nu} = R \left[\frac{1}{m^2} - \frac{1}{n^2} \right] \quad \dots (xi)$$

Comparing, R is found to be equal to $2\pi^2 m e^4 / ch^3$,

$$\text{i.e.,} \quad R = \frac{2\pi^2 m e^4}{ch^3} = 109737 \text{ cm}^{-1}$$

putting the standard values of m , e , c and h .

This excellent agreement of the value of R with the experimental result is indeed a very strong support of the Bohr's theory.

The electron in the hydrogen atom, according to the Bohr's theory, will be in one of the circular orbits around the nucleus; the orbits are characterised by the quantum numbers, $n = 1, 2, 3, 4 \dots$ etc. No energy emission occurs as long as the electron remains in a stationary orbit. But whenever the electron jumps from an outer to an inner orbit, energy is emitted. Thus, whenever an electron jumps down to the orbit $n = 2$ from any outer orbit $n = 3, 4, 5 \dots$, the lines in the Balmer series are obtained. The line H_α in the Balmer series is due to the transition of a electron from the orbit $n = 3$ to the orbit $n = 2$.

On the other hand, a transition of the electron from orbit $n = 4$ to orbit $n = 3$ will produce a line of the Paschen series in the infra-red. If the electron jumps

from orbit $n = 4$ to orbit $n = 1$, it will give rise to a line in Lyman series. In other words, Lyman, Balmer, Paschen, Brackett and Pfund series are formed when electrons jump to orbits $n = 1, 2, 3, 4$ and 5 respectively from outer orbits. This is illustrated in figures V.20 and V.21.

In these calculations it has been tacitly assumed that the nucleus is fixed at the centre of the orbits. But in fact the nucleus (mass M) and the electron (mass m) are rotating about their common centre of mass. It is therefore necessary to replace m in the energy expression (equation ix) by the reduced mass μ , where

$$\mu = \frac{mM}{m+M} = \frac{m}{1 + \frac{m}{M}}$$

The wave number ($\bar{\nu}$) should then be

$$\bar{\nu} = \frac{2\pi^2\mu e^4}{ch^3} \left[\frac{1}{n'^2} - \frac{1}{n^2} \right] = \frac{2\pi^2 m e^4}{ch^3} \cdot \frac{1}{1 + \frac{m}{M}} \cdot \left[\frac{1}{n'^2} - \frac{1}{n^2} \right]$$

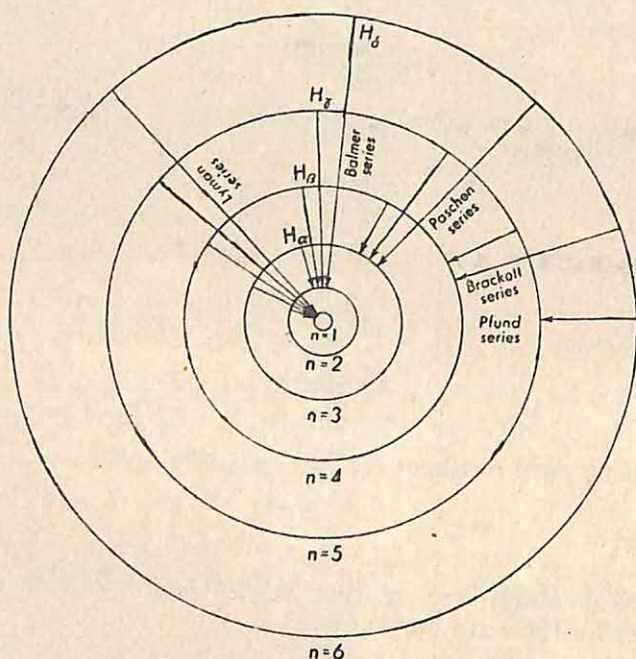


FIG. V.20 Diagrammatic presentation of Bohr orbits of hydrogen atom

i.e., the refined value of the Rydberg constant (R_0) shall be

$$R_0 = \frac{2\pi^2 m e^4}{ch^3} \cdot \frac{1}{1 + \frac{m}{M}} = R \cdot \left(\frac{1}{1 + \frac{m}{M}} \right)$$

Evidently, the Rydberg constant will slightly vary from atom to atom depending upon the nuclear mass. The actual value of R may be determined from atomic spectra. If we consider different hydrogen like structures with one electron revolving round a nucleus of charge Ze , *e.g.*, singly charged He^+ , doubly charged Li^{++} , etc., similar spectral series are obtained. The wave number of these lines will be governed by

$$\bar{\nu} = \frac{2\pi^2\mu e^4}{ch^3} Z^2 \left[\frac{1}{n'^2} - \frac{1}{n^2} \right] = Z^2 R \cdot \frac{1}{1 + \frac{m}{M}} \left[\frac{1}{n'^2} - \frac{1}{n^2} \right]$$

where Z is the atomic number. This has been experimentally established.

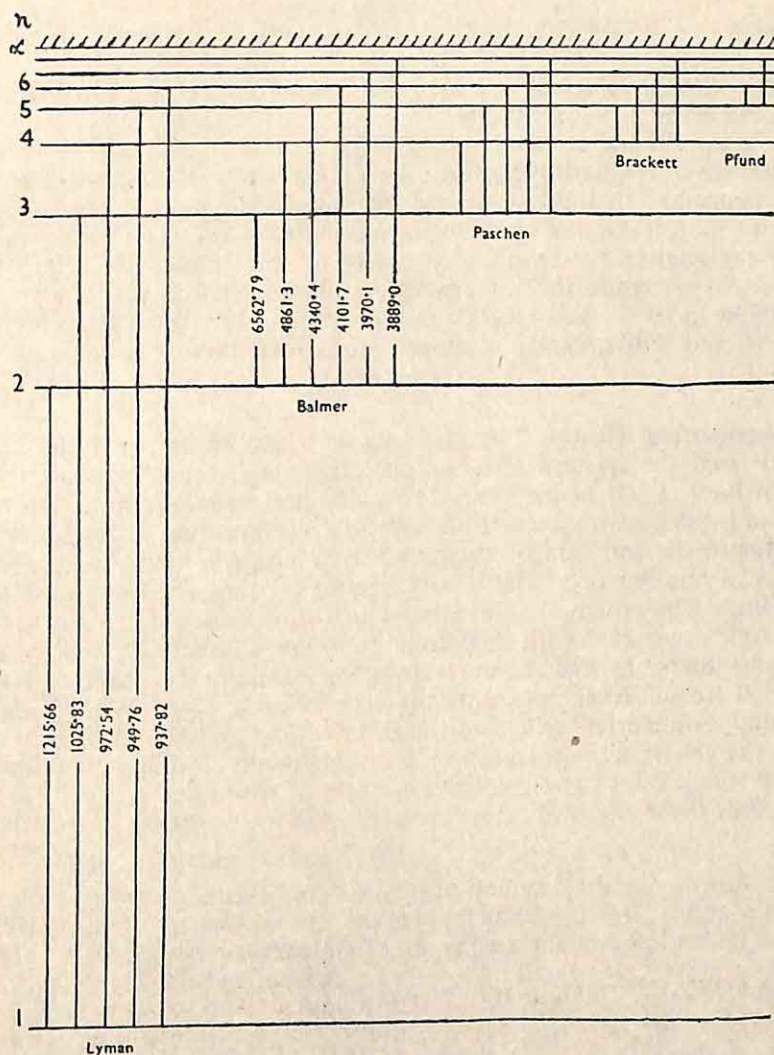


FIG. V.21 Energy levels of hydrogen atom

The Rydberg constants for hydrogen and singly charged helium were experimentally measured ;

$$R_{0H} = R \cdot \frac{1}{1 + \frac{m}{M_H}} ; \quad R_{0He^+} = R \cdot \frac{1}{1 + \frac{m}{M_{He}}}$$

That is,
$$\frac{R_{0H}}{R_{0He^+}} = \frac{1 + m/M_{He}}{1 + m/M_H} = \frac{1 + m/3.97 M_H}{1 + m/M_H}, \quad [\text{since } M_{He} = 3.97 M_H]$$

Substituting the experimental values of R_H and R_{He^+} , it was found that $M_H/m = 1840$ i.e., a proton is nearly 1840 times heavier than an electron.

Ionisation Potential. As energy is absorbed by an atom, the electron moves from the normal inner quantum level ($n = 1$) to outer orbits. The amount of work necessary to remove an electron from its lowest level ($n = 1$) to the infinite distance resulting into the formation of a free ion is called the ionisation potential, measured often in electron-volts. This energy is

$$W = E_f - E_i = \frac{2\pi^2 m e^4}{h^2} \cdot \frac{1}{1 + \frac{m}{M}} \cdot Z^2 \left(\frac{1}{n_\alpha^2} - \frac{1}{n^2} \right)$$

Since $n = 1$, ionisation energy $= \frac{-2\pi^2 me^4 Z^2}{h^2} \cdot \frac{1}{1+m/M} = -RchZ^2 \cdot \frac{M}{m+M}$.

Putting the known values of c , h etc., the ionisation energy of hydrogen is found to be 13.595 eV or 2.18×10^{-11} ergs.

The Bohr theory certainly made an achievement by producing a pictorial representation of the hydrogen atom, which explained the atomic spectral data. But the theory had its limitations and weakness. Attempts to apply the theory to atoms with more than one electron were not successful. The theory did not provide any explanation for union of atoms to produce molecules. The Bohr theory also failed to recognise the wave property of the electron which was established by de Broglie in 1923. As a result, a modification of the theory by Sommerfeld was first made and subsequently a more satisfactory theory from wave-mechanics replaced it.

V.20. Sommerfeld Theory. The necessity of a modification of the Bohr theory stemmed from the spectral observation, under high resolutions, of the different hydrogen lines. Each of the otherwise individual lines was found to consist of a number of hyperfine structure. Bohr's theory interprets the formation of a spectral line as due to the emission of energy when an electron jumps from one quantum orbit (n_1) to another (n_2). The theory cannot account for the multiplicity found in these lines. The obvious explanation which can be mooted is that the electronic energy levels associated with any Bohr quantum number (n) must be more than one. That is, there are several sub-levels in any quantum level, although the energy values of these sub-levels are quite adjacent to each other. With this view in the background, Sommerfeld extended the Bohr's ideas and suggested that

(i) the electronic paths around the nucleus are elliptic with different eccentricities of which Bohr's circular orbit is a special case ; and

(ii) only those elliptical orbits are permitted which satisfy the relations,

$$(a) \oint p_\phi d\phi = kh ; \quad (b) \oint p_r dr = n_r h \quad \dots (1)$$

where p_ϕ and p_r are the angular and radial momenta of the electron with co-ordinates ϕ and r ; h is the Planck constant, ' k ' and ' n_r ' are two positive integers called the azimuthal and the radial quantum numbers respectively (Fig. V.22).

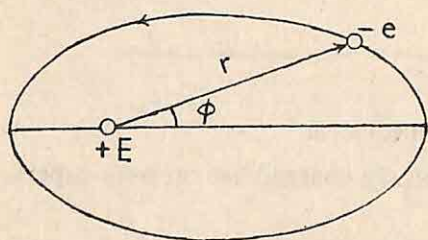


FIG. V.22 Elliptical orbit of the electron

In Bohr's circular orbits, only one co-ordinate, angle ϕ varies periodically but the radius r remains constant. Thus Bohr required only one quantum condition, i.e., $\oint p_\phi d\phi = nh$. In the elliptical motion, both the angle ϕ as also the length of the radius vector r vary periodically as stated above. A mechanical treatment of the electron moving in an elliptical path leads to the following results :

(a) the eccentricity ϵ of the ellipse is related to the quantum number as

$$1 - \epsilon^2 = \frac{k^2}{(k + n_r)^2}$$

But in an ellipse, we know from its geometry that $1 - \epsilon^2 = \frac{b^2}{a^2}$,

where a and b are its semimajor and semiminor axes. It follows,

$$\frac{b}{a} = \frac{k}{k + n_r} = \frac{k}{n}$$

n , being the sum of $k + n_r$, is an integer. The lowest permissible value of k is unity. For, if $k = 0$, b/a will be zero rendering the ellipse into a straight line. The highest permissible value of k is n , so that n_r may be zero, when b/a is unity i.e., the ellipse turns into a circle. The values of k thus range between 1 and n .

(b) The energy of an electron moving in an elliptic orbit is

$$E = -\frac{2\pi^2 me^4 Z^2}{(n_r + k)^2 h^2} = -\frac{2\pi^2 me^4 Z^2}{n^2 h^2}, \quad (Z = \text{atomic number}) \quad \dots (II)$$

This is identical with the expression for the energy of the electron in Bohr's circular orbit of quantum number, n . The energy value is not determined by individual values of k and n_r .

(c) The semimajor and the semiminor axes of the elliptical path are,

$$a = n^2 h^2 / 4\pi^2 m e^2 Z;$$

$$b = n k h^2 / 4\pi^2 m e^2 Z$$

We have now three quantum numbers, n , n_r , and k related as $n = n_r + k$. We may as well do away with one of them, namely n_r , and still define the electronic properties. The quantum number n , which determines the magnitudes of quantised values of energy, is called the *principal quantum number*. We may illustrate the difference between Bohr scheme and Sommerfeld scheme in the following way. Consider an excited hydrogen atom

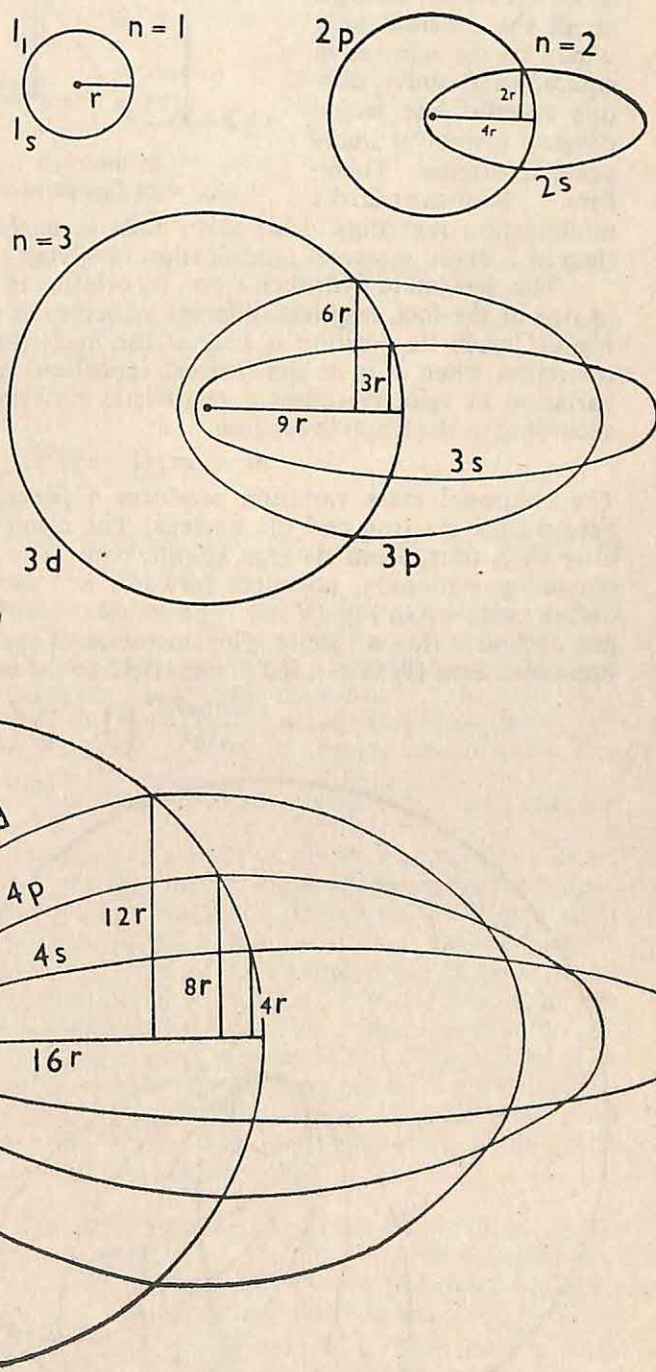


FIG. V.23 Permitted electronic orbits of H-atom

in which the electron is raised to quantum level $n = 3$. Let the electron jump down to level $n = 2$ and produce a Balmer line (Fig. V.24). In Bohr's scheme, a spectral line would originate in just one way, but in Sommerfeld scheme, a line can develop in more than one way.

Since the energy changes in all the different ways would be the same as in equation (II) above, only one spectral line would develop in spite of many possible origins. Therefore, Sommerfeld's

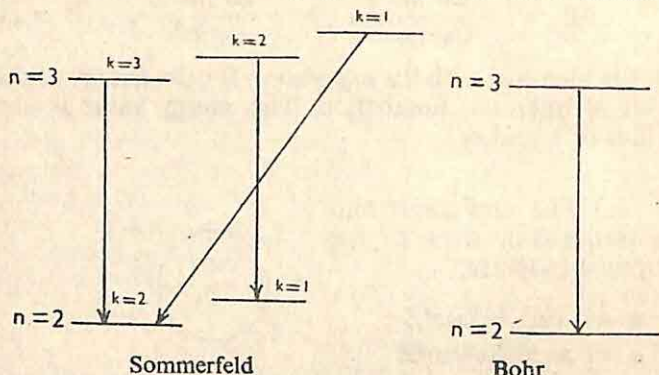


FIG. V.24 Comparison of Bohr & Sommerfeld schemes

modification regarding orbit alone fails to explain the hyperfine structure. He then introduced a second modification involving relativistic corrections.

The electron in hydrogen atom, on orbiting in an elliptic path with the nucleus at one of the foci, acquires different velocities at different points. The velocity is highest when its position is nearest the nucleus (perihelion) and the velocity is minimum when it is at the farthest (aphelion) position from the nucleus. This variation in velocity causes a relativistic variation in the mass of the electron, according to the Lorentz relation

$$m = m_0 (1 - v^2/c^2)^{-\frac{1}{2}}$$

The continual mass variation produces a perturbation in the balancing forces between the electron and the nucleus. The result is that the electron deviates, a little each time, from its true elliptic path. The perihelion position, instead of remaining stationary, advances forward, i.e., precession of the electronic orbit occurs as shown in Fig. (V.25). The actual orbit of the electron around the hydrogen nucleus is thus a rosette. Consideration of such an orbit in terms of the quantum conditions (I) above, led Sommerfeld to the energy value to be

$$E = -\frac{2\pi^2 m_0 e^4 Z^2}{n^2 h^2} \left[1 + \frac{\mu^2}{n^2} \left(\frac{n}{k} - \frac{3}{4} \right) \right]$$

where μ = reduced mass, m_0 = rest mass, of the electron. It is now seen that, unlike the previous result, the electronic energy depends not only on n but also on k (in a small way). Hence the transition of an electron, from $n = 3$ to $n = 2$ of the foregoing example, will not just give one spectral line but a number of closely packed fine lines depending on k -values involved.

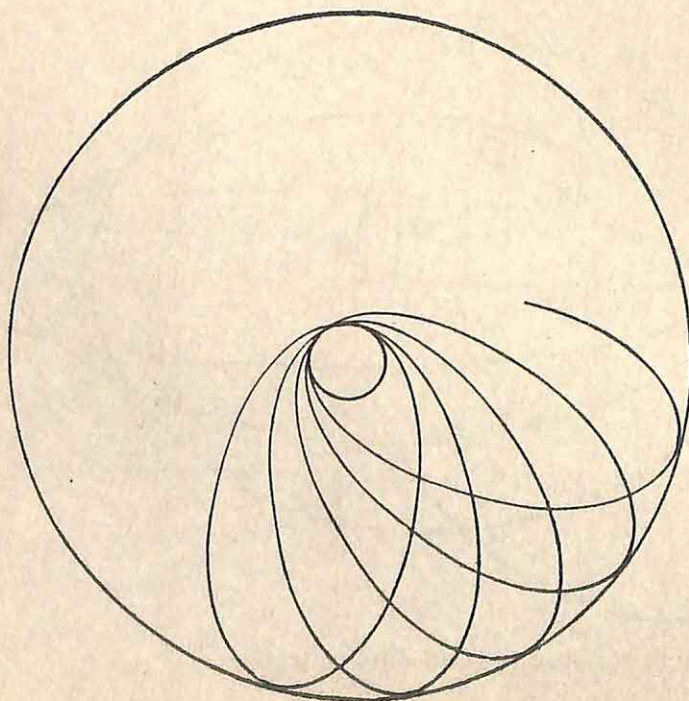


FIG. V.25

V.21. Bohr-Sommerfeld Theory for Complex Atoms. The Bohr-Sommerfeld theory met with formidable difficulties when it was applied to account for

spectral characteristics of poly-electronic atoms. This necessitated additional refinements in the theory ; even then it was not sufficiently universal. We can briefly illustrate this in relation to alkali metal spectra.

Later developments clearly indicated that the azimuthal quantum number k of the Sommerfeld theory could not have integral values 1 to n , but it should be replaced by *orbital angular momentum quantum number*, l , having integral values 0 to $n-1$. An electron whose $l = 0$ is known as *s*-electron. Similarly, an electron, with $l = 1$ is called *p*-electron ; with $l = 2$ is called *d*-electron ; with $l = 3$ is called *f*-electron and so on, irrespective of the principal quantum number, n , of the electron.

Again, we have seen that the energy-value of an electron is quantised as $E = -2\pi^2me^4Z^2/n^2h^2$, the value being negative so long as the electron is within the atom. The electron can also be specified by its *term-value* Γ , which is obtained by dividing the energy value by $-ch$. Thus, the term value Γ of an electron,

$$\Gamma = \frac{2\pi^2me^4Z^2}{n^2ch^3} = \frac{RZ^2}{n^2}$$

where R is the Rydberg constant and n is the principal quantum number having a positive integral value.

Analysis of the alkali metals spectra revealed that the lines formed can be grouped into at least four chief spectral series, namely,

- (i) Sharp series, called *s*-series
- (ii) Principal series, called *p*-series
- (iii) Diffuse series, called *d*-series
- (iv) Fundamental series, called *f*-series

The spectroscopists further established :

(i) Under normal conditions, spectral lines are produced by transitions undergone by valence electrons, *i.e.*, optical electrons.

(ii) Spectral lines in *s*-series involve transition of electrons from a *s*-state to an *p*-state, *i.e.*, l -value changing from 0 to 1. The *p*-series lines are due to transitions of *p*-electrons to *s*-level. The *d*- and *f*-series lines originate from migration of electrons from *d*- to *p*-levels and from *f*- to *d*-levels respectively. The value of n can change by any integral amount but l can alter by ± 1 in such transitions.

(iii) The term value (Γ) of an electron in alkali metals (and also for any polyelectronic atom) is given by $\frac{RZ^2}{(n^*)^2}$ where n^* , the principal quantum number

is found to be non-integral — a fact which strikes at the very root of the Bohr-Sommerfeld idea. The departure of n from integral values depends on the nature of the electron suffering transition. For an *s*-electron, the departure is maximum with gradually diminishing magnitudes for *p*-, *d*- and *f*-electrons. Bohr explained the non-integral quantum number n^* in terms of penetrating and non-penetrating orbits of the electrons. n^* may be considered as $n^* = n - \delta$, where n is the actual integral principal quantum number and δ the deviation, called quantum defect. According to Bohr, the defect arises due to interpenetration of the orbits. The more eccentric elliptical paths of the *s*- and *p*-electrons penetrate deeply into the orbits of the inner electrons, which give rise to precession of the paths as in relativistic effects. It was shown subsequently that such interpenetration of the orbits and the resulting precession would lead to quantum defect.

V.22. Electronic Spin and Spin Quantum Number. A closer examination of the atomic spectra demanded further refinements of the theory. It was soon found that under high resolution, the spectral lines of the alkali metals had fine structures. The common yellow line of sodium in the principal series consists of two fine lines $5889.96 \text{ \AA}$ and $5895.93 \text{ \AA}$, *i.e.*, differing by about $6 \text{ \AA}$. This suggests that one or both the energy levels occupied by the optical electron before and after the jump should at least be a close doublet, thus enabling the electron to execute more than one type of transition accompanied by emission of *almost* same amount of energy.

Uhlenbeck and Goudsmit (1925) proposed that the electrons spin about an axis like a top, and consequently, have *spin angular momentum* (called spin-moment) in addition to their angular momentum due to orbital motion.

Sommerfeld originally expressed orbital angular momentum as $p_\phi = k \cdot \frac{h}{2\pi}$.

It was subsequently corrected and modified to the form $p_l = \sqrt{l(l+1)} \cdot \frac{h}{2\pi}$.

The spin angular momentum was also supposed to be quantised and expressed in the form,

$$p_s = \sqrt{s(s+1)} \cdot \frac{h}{2\pi}$$

where s is the *spin quantum number* having the value, $s = \frac{1}{2}$.

Both p_l and p_s are angular momenta and can be vectorially added to give the total angular momentum p_j as $\vec{p}_j = \vec{p}_s + \vec{p}_l$.

p_j has also quantised values, such that $p_j = \sqrt{j(j+1)} \cdot \frac{h}{2\pi}$

where j is the mechanical moment quantum number. Its values are, for systems with one valence electron,

$$\begin{aligned} j &= l+s \text{ or } j = l-s, & \text{when } l > s \\ j &= s+l \text{ or } j = s-l & \text{when } l < s \end{aligned}$$

This means that for a given pair of values for l and s of the valence electron of the alkali metal, p_j can have two possible magnitudes for the two possible values of j . Since p_j is the vector sum of p_s and p_l the two permissible values of p_j can occur only if p_l and p_s be oriented in two distinct and definite ways—parallel and antiparallel. When the component of $\vec{p}_s$ ($= s \cdot \frac{h}{2\pi}$) is along the $\vec{p}_l$ direction it is parallel and when the component is in the direction opposite to $\vec{p}_l$ it is antiparallel and is equal to $-s \frac{h}{2\pi}$ (see Fig. V.26).

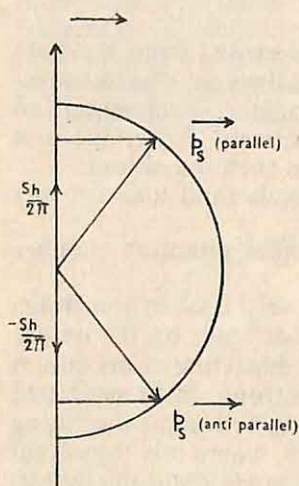


FIG. V.26

Thus, for $l = 2$ and $s = \frac{1}{2}$, j can have values $5/2$ and $3/2$. But for an s -level electron, where $l = 0$ both the j -values are the same. That is, an s -level is a singlet, but p -level is a doublet, and so are the d -levels and f -levels. The following scheme represents the doublet nature of the sodium yellow line (Fig. V.27). It is thus seen that the energetics of the electron in an atom can be explained with quantum numbers n , l , s and j ; where j , of course, can be substituted in terms of l and s .

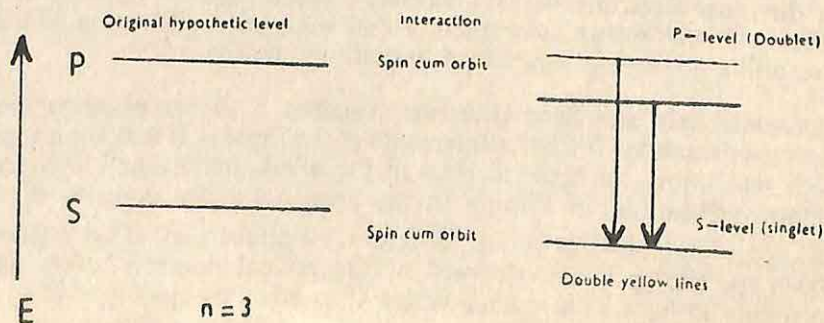


FIG. V.27 Double yellow lines of sodium ($n = 3$)

V.23. Magnetic Quantum Number. When the atomic spectra are produced in presence of an external magnetic field, the spectral lines are split up into further fine structures. For example, the yellow doublet of sodium mentioned earlier yields altogether ten fine structure lines when the spectrum is obtained in a magnetic field of, say, 10000 gauss. Such splitting is called *Zeeman Effect* after the name of its discoverer (1896). Any theory of atomic structure must necessarily be capable of explaining the magnetic fine structure levels.

When the atom is placed in a magnetic field (say, intensity H) the spinning electrons because of their magnetic moments will experience torques and will be oriented. Suppose the field is applied in the direction of Z -axis; the Sommerfeld orbits (modified by spinning effects) become space oriented. The orbits can take up only certain quantised orientations in space making discrete angles with the vertical (Fig. V.28).

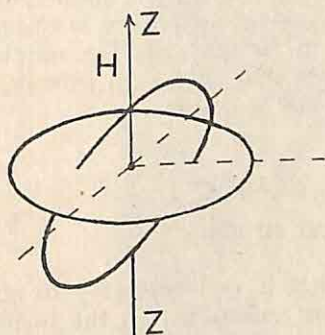


FIG. V.28

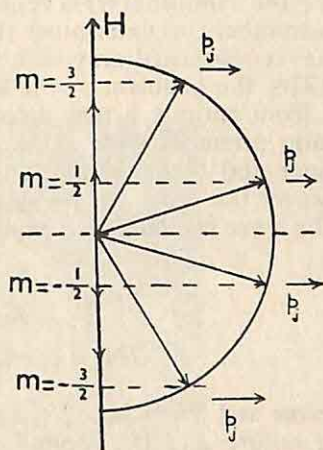


FIG. V.29

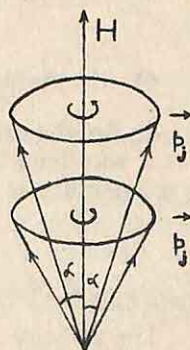
This, known as space quantisation, is due to the interaction between the externally applied magnetic field and the magnetic fields of the rotating and spinning electron. Now, for a monovalent system, the direction of the p_j vector would be related to the spatial extension of the Bohr-Sommerfeld orbit. Therefore, space quantisation of the electron orbit in a magnetic field would correspondingly mean the space quantisation or possible discrete settings of the p_j vector in space. For these p_j settings we need an additional quantum postulate such that the orientations would have components of p_j along the external field direction equal to

$$p_z = p_j \cos \alpha = m \cdot \frac{h}{2\pi}$$

m is called the magnetic quantum number. It can take up values from $-j$ to $+j$, i.e., $-j, -j+1, -j+2 \dots 0, 1, 2, 3, \dots j-1, j$. The total number of such settings would be $(2j+1)$. Hence for $j = 3/2$, the number of p_j orientations would be 4. Pictorially this is illustrated in Fig. V.29.

Calculations, involving the precession of p_j , around the field direction H , introduce several possible variations, dependent on m -values, in the electronic energy levels. These variations account for the fine structure levels (Zeeman levels) of monovalent systems in a magnetic field. Extension of such precession ideas to polyvalent atoms as well has met with success.

It will be noted that the space-quantisations of the core electrons have not been considered. This is because they are internally all space-oriented in their own mutual magnetic fields in such a way that a complete neutralisation

FIG. V.30 Precession of p_j around H

of the effective magnetic field due to the core occurs. They are thus indifferent to any applied external magnetic field.

We thus find that refinements, including the concept of spinning electrons, and space-quantisation in magnetic field, have to be superimposed on the Bohr-Sommerfeld orbital model modified by the idea of perturbation and precession. This structure utilising various vector quantities of the atom together with some quantum-mechanical relations constitutes the frame-work of what is known as the theory of "vector model of atom".

The electronic properties, viz., energy-values, term-values, etc. are seen to be governed by a set of five quantum numbers n, l, s, j and m of which j can be substituted by $l + s$ or $l - s$. In effect, we have to reckon with four quantum numbers, n, l, s and m in the theory of atomic structures. It can be generally stated: the principal quantum number (n) determines principally the size and energy of the orbit; the azimuthal (l) is responsible for the shape of the orbit; the magnetic quantum number (m) determines the orientation of the orbit, while spin quantum number (s) is concerned only with the spin of the electron.

In 1926, the problem of the mechanics of atomic structure was successfully attacked from entirely a new direction based on more rigid mathematical basis. Here again, attempts were made in two ways—through *wave mechanics* due to Schrödinger and through *matrix mechanics* of Heisenberg. The ultimate results were however the same. In the next section we shall only deal with the bare outlines of the wave mechanics to explain the atomic structure.

F. WAVE MECHANICS

(New concept of atomic structure)

V.24. Waves and Particles. We have seen that it was necessary to accept both the wave nature and the atomistic nature in radiations. In the phenomena of interference and diffraction, the radiations must be regarded as waves, whereas the photo-electric effect, Compton effect etc. are explainable only in terms of quanta of radiations.

According to Louis de Broglie (1923), this dual nature—wave and particle—should not be confined to radiations alone but should also be extended to matter. He suggested that electrons, protons, atoms, etc. could not be regarded simply as corpuscles but that periodicity of wave motion must also be assigned to them. de Broglie was led to this hypothesis from consideration of quantum theory and the special theory of relativity. He also proposed a relation between momentum and wavelength of a particle in motion. In considering light of frequency ν , we know the energy is given by $\epsilon = h\nu = h \cdot \frac{c}{\lambda}$; (λ = wave length, c = velocity of light). Again, from the theory of relativity, $\epsilon = mc^2$, (m = mass of photon).

Combining these two relations, we have

$$mc = h/\lambda$$

$$\text{or the momentum, } p = \frac{h}{\lambda}, \quad \text{i.e., } \lambda = \frac{h}{p}$$

de Broglie extended this relation into the dynamics of a particle and proposed that a wavelength λ is associated with a particle in motion, which is related to its momentum as

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \dots (a)$$

where m is the total mass of the particle and v its velocity.

The velocity v (a particle property) is thus connected to wavelength λ (a wave property) by Planck's constant h . The validity of this hypothesis, i.e., the existence of waves associated with particles, was then demonstrated experimentally by Davisson & Germer (1927) and by G. P. Thomson (1928).

If the particle is an electron and if it is subjected to a potential difference V so as to acquire a velocity v , ($v \ll c$) then,

$$Ve = \frac{1}{2}mv^2, \text{ hence } \lambda = \frac{h}{\sqrt{2mVe}} \quad \dots (b)$$

In the experimental arrangement, narrow beams of electrons coming out from a hot filament or a cathode ray tube were led through a high potential and then passed through thin metal films. Finally they were received on a photographic plate, where diffraction patterns similar to those produced by X-rays were obtained. This proves that waves are associated with beams of electrons. Subsequently such diffraction patterns were also produced with beams of neutrons or hydrogen atoms, i.e., relatively massive particles have also wave properties. Quantitative measurements from these diffraction rings showed that the observed wavelengths are

those given by the de Broglie relation, $\lambda = \frac{h}{mv}$.

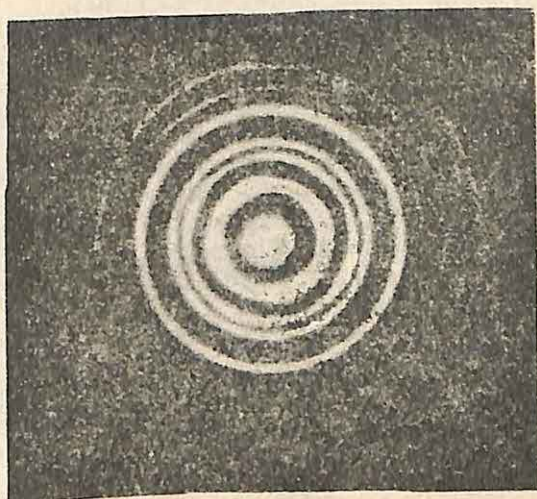


FIG. V.31 Electron beam diffraction pattern

Now if an electron be accelerated through a potential difference of 100 volts, then its wavelength,

$$\lambda = \frac{h}{\sqrt{2mVe}} = 1.2 \text{ \AA}, \quad (m = 9.1 \times 10^{-28} \text{ gms})$$

But if a bullet of 2.2 gms be shot out with a velocity of 3×10^4 cm/sec the wavelength associated with it would be

$$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-27}}{2.2 \times 3 \times 10^4} = 1 \times 10^{-28} \text{ cm}$$

which is too small to be of any consequence and would not come into our observation.

We thus see that an electron seems to behave partly as a wave and partly as a particle. But how should we visualise the electron; is it a particle or is it a wave? It is quite difficult to reconcile the two concepts. An understanding of the mutual relationship between the particle and wave concepts have been possible by Heisenberg's 'Uncertainty Principle', which is now a fundamental principle of physics.

In classical physics and in classical quantum theory, the precise and simultaneous determinations of momentum (velocity), position, path of microscopic particles are permissible. But is this really possible?

In visualising a particle, we conceive it as something possessed of definite momentum, energy and definite position, etc., at any particular time. Heisenberg made the assertion that by no means whatsoever, real or imaginary, can we simultaneously determine the exact magnitude of momentum and the exact position at any time. To illustrate : Suppose we want to locate the exact position of an electron with the help of blue light. The attempt will fail as the wave-length of the blue light is million times larger than the diameter of the electron. We are, therefore, required to use a radiation of much shorter wave-length, (say X-rays). The electron particle will then be located through the scattering of X-rays. But in the scattering, the electron will be accelerated due to Compton effect. The result will be a change in its momentum and the value of momentum will be uncertain. The shorter the wavelength used the worse is the uncertainty in momentum. This uncertainty either of position or of momentum is not merely due to imperfectness of experimental technique. There is always something inherent in the very nature of instrument which interacts with the system under study and defeats our purpose of ascertaining definite position and also momentum simultaneously.

In the diffraction experiments with electron beams, we can measure the wavelength and can determine definitely the momentum of an electron by de Broglie relation. But then the position of an electron will be indefinite. For, if we select out one single electron from the beam, it will scatter away from the crystal, but the direction and the angle at which the electron is going to be scattered is quite uncertain. Moreover in applying the wave concept to a single electron it is depicted as a small packet of waves extending over a small region Δd . We can then only say that it is somewhere within the packet which extends over Δd . The exact position of the electron at any instant of time (t) is not known. In no one single experiment can we demonstrate both the particle and the wave property of the system under observation. Indeed wave and particle properties complement each other in the full description of a process, not necessarily indicating thereby that the system is both a particle and a wave *i.e.*, dual in character. Heisenberg also pointed out that like position and momentum, other pair of properties such as energy and time cannot also be simultaneously and precisely determined.

Suppose we attempt to determine accurately the position of an electron with a microscope of high resolving power. Since resolution depends on the wavelength of light used, let us use the shortest wavelengths, such as γ -rays, having a frequency ν . It can be shown that the position of the electron is known within an amount Δx , such that $\Delta x = \lambda/\sin \alpha$, where 2α is the vertical angle of the cone of light coming from the object (Fig. V.32). The uncertainty in the determination of the x -coordinate of the position of the electron is thus Δx . The radiation reaching the objective of the microscope must have been scattered by the electron and the electron has suffered a recoil (Compton effect), the momentum change being $h\nu/c$. The scattered radiation can enter the microscope anywhere within the angle 2α of the cone, the momentum change in the x -direction

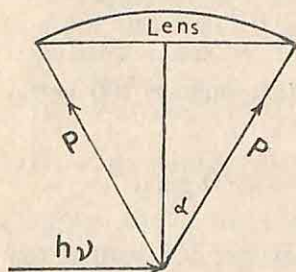


FIG. V.32 Illustration of uncertainty principle in the observation of a particle under microscope

is given by $\frac{h\nu}{c} \sin \alpha$. This is uncertain to the amount

$$\Delta p \approx \frac{h\nu}{c} \sin \alpha.$$

The net uncertainty in the simultaneous determination of position and momentum of the electron is given by their product ;

$$\Delta x \cdot \Delta p = \frac{\lambda}{\sin \alpha} \cdot \frac{h\nu \sin \alpha}{c} \approx h, \quad (\text{since } c = \nu\lambda).$$

This is the quantitative expression of the uncertainty principle of Heisenberg (1927). It can also be expressed in terms of energy and time,

$$\Delta E \cdot \Delta t \approx h$$

Suppose a cricket-ball of 200 gms is flying with a speed of 10 metres per second, i.e., momentum $p = 200 \times 1 \times 10^3 = 2 \times 10^5$. To ascertain this within 0.1 %, Δp will not exceed $2 \times 10^5/10^3 = 2 \times 10^2$. The uncertainty in respect of its position $\Delta x = h/\Delta p = 6.6 \times 10^{-27}/2 \times 10^2 = 3.3 \times 10^{-29}$ which is certainly too small to be detected. The principle of Heisenberg is therefore unimportant for a macroscopic body.

But if we take an electron moving in an atom ($v = 2 \times 10^8$ cm/sec) its momentum, $p = 2 \times 10^8 \times 9 \times 10^{-28} = 18 \times 10^{-20}$. Even if we know this within 1 %, $\Delta p = 18 \times 10^{-20}/10^2 = 1.8 \times 10^{-21}$. The uncertainty of its position $\Delta x = 6.6 \times 10^{-27}/1.8 \times 10^{-21} = 3.7 \times 10^{-6}$ cms. That is, it is not known even if at the given instance, the electron is within the atom or not. Herein lies the significance of the principle implicitly demonstrating the inadequacy of the Bohr postulate.

V.25 The Schrödinger Wave Equation. The acceptance of the uncertainty principle means that the old mechanics has to be discarded, since it is no longer possible to assign a definite position and momentum to a particle. The discrepancy is not serious for objects of appreciable size, but for minute particles like electrons, atoms etc., a new mechanics must be used in which a function is employed whose square would express the probability of a particle of given momentum being at a given point, since it is not possible to say that it is at the point. This new mechanics is based on the fundamental equation proposed by Schrödinger.

Schrödinger starts by considering the dynamical equation for the propagation of elastic waves. Let us first take the simplest type of wave motion, that of a stretched string. If u be the velocity of the wave, and if w is the amplitude at any point of co-ordinate x at time t then the equation for wave motion is given by,

$$\frac{\partial^2 w}{\partial x^2} = \frac{1}{u^2} \cdot \frac{d^2 w}{dt^2} \quad \text{.....(a)}$$

w is a function of the co-ordinate x and of time t so that

$$w = \psi(x)\phi(t)$$

In the case of a stretched string, $\phi(t) = A \sin 2\pi vt$, v is its frequency. We can thus write,

$$w = \psi(x) A \sin 2\pi vt$$

i.e.,

$$\frac{\partial^2 w}{\partial t^2} = -\psi(x) 4\pi^2 v^2 (A \sin 2\pi vt) = -\psi(x) 4\pi^2 v^2 \phi(t)$$

Also from (b)

$$\frac{\partial^2 w}{\partial x^2} = \frac{\partial^2 [\psi(x)]}{\partial x^2} \cdot \phi(t)$$

Substituting in (a), the equation for elastic waves,

$$\left. \begin{aligned} \frac{\partial^2 [\psi(x)]}{\partial x^2} &= -\frac{4\pi^2 v^2}{u^2} \cdot \psi(x) \\ \text{or} \quad \frac{\partial^2 [\psi(x)]}{\partial x^2} &= -\frac{4\pi^2}{\lambda^2} \cdot \psi(x) \end{aligned} \right\} \quad \text{.....(d)}$$

since the velocity $u = v\lambda$, λ being the corresponding wave length. If the wave motion is extended to include all the three co-ordinates x , y and z , when $\psi(x)$ shall be replaced by $\psi(x, y, z)$, the wave equation takes the form,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} \psi,$$

ψ is written in place of $\psi(x, y, z)$ for simplicity and it represents the amplitude function for the three co-ordinates. The terms on the left-hand side may be replaced by the Laplacian operator $\nabla^2 \psi$ and the wave-equation is expressed as

$$\nabla^2 \psi + \frac{4\pi^2}{\lambda^2} \psi = 0 \quad \text{.....(V.2)}$$

This is a general relation for all systems. If we now consider the minute particles like electrons and use de Broglie relation $\lambda = h/mv$, we have

$$\nabla^2 \psi + \frac{4\pi^2 m^2 v^2}{h^2} \psi = 0 \quad \dots (V.3)$$

If E is the total energy and V , the potential energy of the particle, then its kinetic energy, $\frac{1}{2}mv^2 = E - V$. Therefore,

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \dots (V.4)$$

This relationship is the Schrodinger Wave equation which is at the basis of our understanding the atomic and molecular structures.

V.26. Interpretation of ψ . In the theory of propagation of light waves, the intensity of the light at any point is proportional to the square of the displacement of the wave at that point. Considered from the view-point of photons, the intensity should be proportional to the number of photons arriving at the point per second. But this number density of the photons is a measure of the probability of the occurrence of photons at the given point. We can therefore say that the probability of the occurrence of photons in a region is proportional to ψ^2 , the square of the wave amplitude of a wave equation. It is not necessary to consider the trajectory the photons pursued to arrive at the spot.

Extending this idea to electron beams, the probability of an electron being found at a given small volume is proportional to $\psi^2 dv$, where ψ is the displacement function of the associated de Broglie waves at the spot of small volume dv . The wave function ψ of Schrödinger equation is thus a state function, the square of which (ψ^2) has a physical meaning related to probability. The purpose of the wave equation thus seems to be to provide statistical information about the place where the electrons are likely to be detected. We may then conclude that the radiations and the so called fundamental particles are particles in the Heisenberg sense, their motions being governed by wave laws, although we do not know about their actual trajectory. This description of matter and radiation is equivalent to saying that particle behaviour and wave behaviour complement each other in the attainable full description of a mechanical process. This probability interpretation of ψ^2 is due to Born. Schrödinger however adduced a different physical significance to ψ^2 , assuming that $\psi^2 dv$ would denote the charge density of the electrons in an atom within the region dv . That is, the electron is to be regarded as 'smeared out' into a cloud of electricity having different densities at different points.

In the physical interpretation of the wave function as probability amplitude, it is necessary for it to be governed by some mathematical conditions. If $\psi(x)$ be a solution of the wave equation for an electron, (only x -coordinate considered), the probability of its existence in the range x and $x+dx$ is given by $\psi^2(x)dx$. It is a mathematical necessity that $\psi(x)$ should be single-valued, finite and continuous for all physically possible values of x .

Eigenvalues and Eigenfunctions :

In tackling a physical problem—such as formation of standing waves in a stretched string fixed at two points—one has often to deal with a differential equation characteristic of the problem. The mathematical solutions of the differential equation are numerous, not all of which are suitable solutions for the physical problem.* We have therefore, often to choose and select suitable solutions which would be acceptable for the physical problem. Such acceptable solutions are obtained if certain parameters occurring in the differential equation take up proper

* This is due to the fact that certain demands, depending on the problem, are placed on the nature of the solutions e.g., in the case of vibration of strings, the demands on the solutions are that the latter are to vanish at the two points where the string is fixed. In systems where Schrödinger equation is applied, the demands are that ψ (the solutions) should be finite, continuous and single-valued.

values. These proper values of the parameters are called *eigenvalues* corresponding to each of which there occurs a suitable solution called *eigenfunction*. In the wave equation for the vibration of string, it is the wavelength parameter (which occurs in the velocity factor u) that takes up suitable eigenvalues and for each wave length eigenvalue, one obtains a proper solution or eigenfunction.

The acceptable solutions (*i.e.*, eigenfunctions) of Schrödinger equation are obtained if the energy parameter occurring in the equation takes up proper values *i.e.*, eigenvalues. Sometimes, depending on the problem, the permissible eigenvalues are continuous and it is said to have a continuous energy eigenvalue. Sometimes, again, the permissible energy eigenvalues are discrete and the energy of the system is then said to be quantised.

V.27. Solution of Wave Equation. The solution of a wave-equation is highly involved. We shall only deal here qualitatively a few very simple cases, omitting details.

The simplest case will be the wave equation for a free particle, *i.e.*, where potential $V = 0$. Hence, in one dimension, the equation is,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}E\psi = 0.$$

A solution satisfying the equation is,

$$\psi = A \sin \left(\sqrt{8\pi^2mE/h^2} \cdot x \right) \quad \dots (i)$$

($A = \text{constant}$).

For every positive value of E , the right-hand side yields single-valued, finite and continuous quantities. Hence, this is a solution of the wave equation, as can be seen by direct substitution. In this case, for all +ve values of E , the free particle would show a continuity of energy states.

Particle in a Box. Now suppose the motion of the particle is restricted between two fixed boundaries. Consider first the motion along x co-ordinate only. For values between $x = 0$ and $x = a$, the particle is free ($V = 0$). At the boundaries $x = 0$ and $x = a$ the particle is stopped with barriers of high potential, $V = \infty$. When the particle is thus confined between the two limits, the de Broglie waves, (as in the case of standing waves of stretched string), should have an *integral* number of half-wave lengths between 0 and a , *i.e.*, $a = n\lambda/2$. The figures (5.32a) and (5.32b) indicate the potential barrier and the allowed electron waves.

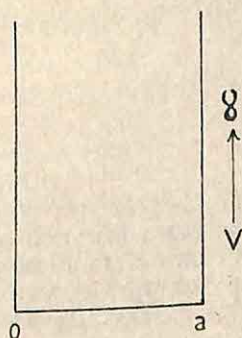


Fig. V.32a

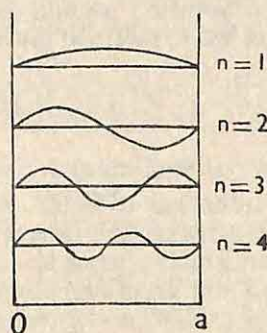


Fig. V.32b

At the two ends, ψ should be zero. When $x = 0$ it is evident from equation (i) above, $\psi = 0$. And also when $x = a$, ψ should become zero, only if

$$\sqrt{8\pi^2mE/h^2} \cdot a = n\pi$$

$$\text{i.e., if} \quad E = n^2h^2/8ma^2 \quad \dots (ii)$$

where n is an integer.

It is clear that with increase in ' a ' the kinetic energy of the electron decreases. Further, the integer n is a quantum number, indicating the number of nodes in the

wave. If $n = 1$, number of nodes = 0 ; if $n = 2$, number of nodes = 1 and so on. The energy is proportional to n^2 .

If we now consider the motion in three dimensions, the expression for energy will take the form,

$$E = \frac{h^2}{8m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right]$$

We are indeed considering a particle moving in a box of dimension (a, b, c) . This is often referred to as a case of 'particle in a box'. Three quantum numbers (n_x , n_y and n_z) are introduced for the motion in three dimensions. It further shows that the motion of a particle in a box with restrictions is quantised.

V.28. The Wave Mechanical Treatment of H-atom. We can now attempt a qualitative description of the quantum mechanical treatment of the hydrogen atom, which would reveal features enabling one to form ideas about atomic structures. In the hydrogen atom, the single electron of charge $-\epsilon$ rotates round the central proton

of charge $+\epsilon$. The potential is $V = \frac{-\epsilon^2}{r}$. The Schrödinger equation then can be expressed as,

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} \left[E + \frac{\epsilon^2}{r} \right] \psi = 0 \quad \dots (A)$$

Generally this equation is transformed into polar co-ordinates (r, θ, ϕ) from the Cartesian co-ordinates for its solution

$$\psi = R(r) \Theta(\theta) \Phi(\phi)$$

The equation then takes the form

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{d\psi}{dr} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{8\pi^2 m}{h^2} \left(E + \frac{\epsilon^2}{r} \right) \psi = 0 \quad \dots (B)$$

The solution of this equation, which is complicated, has been attempted in the formal fashion of solving second order differential equation. Subject to the conditions that ψ solution should be finite, single-valued and continuous, discrete energy values were obtained given by the expression,

$$E = -\frac{2\pi^2 m e^4}{n^2 h^2} \quad \dots (C)$$

where n is a positive integer.

This is identical with the expression for energy in Bohr theory. It was not necessary, in solving Schrödinger equation, to make any additional assumption. The quantum number n has appeared naturally as a result of solution of the wave equation and the Bohr's arbitrary postulate is unnecessary. The wave function ψ is also called *orbital* in chemistry since its knowledge indirectly gives us an idea about electronic charge distribution, a wave-mechanical substitute for electronic orbit of quantum theory. An analysis of ψ , or more specifically of R , shows that the most probable positions of the occurrence of electrons around the nucleus coincide with the specific Bohr orbits.

The complete solution of the wave equation introduces, apart from n the principal quantum number, two other integral parameters, namely l and m , the azimuthal quantum number and the magnetic quantum number. l can take up integral values from 0 to $n-1$ and m can have integral values from $-l$ to $+l$.

For the ground state of the hydrogen atom, the orbital depends only on the radial co-ordinate (r) and is independent of θ and ϕ . The graphical representation of ψ against angular variables θ and ϕ would be spherically symmetrical as in

Fig. V.33(a). Such orbitals are called *s*-orbitals. In the excited states of H-atom, ψ may depend upon θ and ϕ and in consequence the cloud-charge distribution may be oriented symmetrically about *x*-, *y*- and *z*-axes. These are *p*-orbitals (Fig. V.33b). Similarly we have other differently oriented orbitals called *d*- and *f*- orbitals.

The wave-mechanical treatment thus establishes :

(a) the electronic energy levels are quantised,

(b) the parameters n , l and m have integral values and correspond to the quantum numbers of the old quantum theory.

(c) the different charge cloud distributions corresponding to *s*, *p*, *d*, *f* etc., exist indicating the shape or structure of the atom.

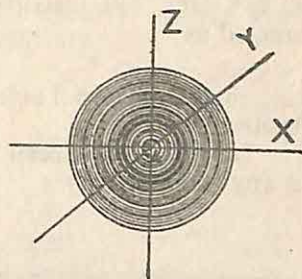


FIG. V.33a

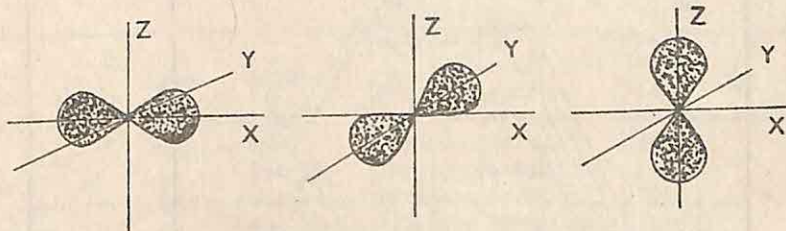


FIG. V.33b

The mathematical solution of wave equation was not enough to explain the entire spectral character. The concept of the spinning electron was necessary. Arbitrary spin wave function α or β has to be used in addition to ψ -function. The spin moments of the electron along the direction of the externally applied magnetic field are given the values $\frac{sh}{2\pi}$ and $\frac{-sh}{2\pi}$ where $s = \frac{1}{2}$; and s is the fourth quantum number called *spin quantum number*.

V.29. Pauli's Exclusion Principle. We have seen that the state of an electron in the atom is specified by four quantum numbers, n , l , m and s . Pauli (1925) introduced a principle for the assignment of quantum numbers to the electrons, known as "*Pauli's Exclusion Principle*". This principle states that *no two electrons in an atom can exist in the same quantum state*. It means that no two electrons in a given atom can have four quantum numbers the same.

Electrons with the same value for principal quantum number n form a definite group or shell. These groups or shells have been designated as *K*-shell, *M*-shell etc. ..., following *X*-ray notations.

According to the value of orbital angular momentum l , electrons in a given shell are further subdivided into subgroups. The maximum number of subgroups in a given shell of value n is n . The maximum number of electrons in a subgroup depends upon the possible values of m and s . It can be shown that the highest number of electrons that can occur in a subgroup is $2(2l+1)$. We know that l can have a value from 0 to $n-1$. The different subgroups are represented by small letters *s*, *p*, *d*, *f*, *g* ... etc., as

$$l = 0, 1, 2, 3, 4, \dots$$

$$s \quad p \quad d \quad f \quad g \quad \dots$$

In the table below are given the assignments of maximum possible number of electrons in the first three shells (*K*, *L*, *M*) with $n = 1, 2$ and 3.

All the electrons within a subgroup of a shell have same n and l -values and are called *equivalent electrons*. An electron in a shell for which $l = 0$ is called an *s*-electron, for $l = 1$ a *p*-electron and so on. In denoting the number and position of electrons, it is usual to write the number of the shell as a prefix to the letter representing its l -value. The number of electrons with same n and l -values is indicated by an index at the upper right of letter expressing l -value. Thus two *s*-electrons

of the *K*-shell are written as $1s^2$, four electrons of the *L*-shell with $l = 1$ are written as $2p^4$, etc. The distribution of the 12 electrons of the Magnesium atom is expressed as

$$1s^2.2s^2 2p^6.3s^2$$

i.e., there are two $1s$ -electrons, two $2s$ -electrons and six $2p$ -electrons and two $3s$ -electrons.

It will also be seen that the maximum number of electrons accommodated in any shell is $2n^2$.

TABLE
ASSIGNMENT OF ELECTRONS IN GROUPS

Shell	Quantum numbers				No. of electrons in Subgroup	No. of electrons in completed shell
	<i>n</i>	<i>l</i>	<i>m</i>	<i>s</i>		
K	1	0	0	$+\frac{1}{2}$	2	2
	1	0	0	$-\frac{1}{2}$		
L	2	0	0	$+\frac{1}{2}$	2	8
	2	0	0	$-\frac{1}{2}$		
	2	1	-1	$+\frac{1}{2}$	6	
	2	1	-1	$-\frac{1}{2}$		
	2	1	0	$+\frac{1}{2}$		
	2	1	0	$-\frac{1}{2}$		
	2	1	1	$+\frac{1}{2}$		
	2	1	1	$-\frac{1}{2}$		
M	3	0	0	$+\frac{1}{2}$	2	18
	3	0	0	$-\frac{1}{2}$		
	3	1	-1	$+\frac{1}{2}$	6	
	3	1	-1	$-\frac{1}{2}$		
	3	1	0	$+\frac{1}{2}$		
	3	1	0	$-\frac{1}{2}$		
	3	1	1	$+\frac{1}{2}$		
	3	1	1	$-\frac{1}{2}$		
	3	2	-2	$+\frac{1}{2}$	10	
	3	2	-2	$-\frac{1}{2}$		
	3	2	-1	$+\frac{1}{2}$		
	3	2	-1	$-\frac{1}{2}$		
	3	2	0	$+\frac{1}{2}$		
	3	2	0	$-\frac{1}{2}$		
	3	2	1	$+\frac{1}{2}$		
	3	2	1	$-\frac{1}{2}$		
	3	2	2	$+\frac{1}{2}$		
	3	2	2	$-\frac{1}{2}$		

V.30. The Periodic Table of the Elements. The periodic table, drawn up by the chemists primarily from the chemical properties of the elements, was shown to be fundamentally based on the atomic numbers (*Z*). The atomic number, which represents the net positive charge of the nucleus, is also the numerical position in the arrangement of the elements in the Table. This also equals the number of electrons surrounding the nucleus when the atom is in its normal neutral condition. The chemical properties depend upon the nuclear charge or the number of circumnuclear electrons. The problem of the Periodic Table really involves the correlation of physical and chemical properties with the arrangement of electrons in the atom.

In Fig. V.34 is given Bohr's arrangement of the elements in the Periodic Table upto uranium, based on atomic number. The arrangement assures that there are no unknown gaps in it and there is no other incongruity.

Period	Group	Element	Period	Group	Element	Period	Group	Element	Period	Group	Element
I	(1s)	1 H	IV	(4s)	19 K	V	(5s)	37 Rb	VII	(6s)	55 Cs
		2 He			20 Ca			38 Sr			56 Ba
II	(2s)	3 Li			21 Sc			39 Y			57 La
		4 Be	III	(3s)	11 Na			40 Zr			58 Ce
		5 B			12 Mg			41 Nb			59 Pr
		6 C			13 Al			42 Mo			60 Nd
		7 N			14 Si			43 Tc			61 Pm
		8 O			15 P			44 Ru			62 Sm
		9 F			16 S			45 Rh			63 Eu
		10 Ne			17 Cl			46 Pd			64 Gd
					18 Ar			47 Ag			65 Tb
								48 Cd			66 Dy
								49 In			67 Ho
								50 Sn			68 Er
								51 Sb			69 Tm
								52 Te			70 Yb
								53 I			71 Lu
								54 Xe			72 Hf
											73 Ta
											74 W
											75 Re
											76 Os
											77 Ir
											78 Pt
											79 Au
											80 Hg
											81 Tl
											82 Pb
											83 Bi
											84 Po
											85 At
											86 Rn

FIG. V.34 Bohr's Periodic Table

It is clear from the groupings in the Table that the occurrence of an inert gas at intervals is the turning point in the properties of the elements as we proceed with increasing atomic numbers. Rydberg showed that a simple numerical expression can be used for the atomic number of the inert gases, as

$$Z = 2 [1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2 + 4^2 + \dots]$$

so that, He = 2, Ne = 10, Ar = 18, Kr = 36, Xe = 54, Rn = 86. The existence of this series suggested that the electrons occur probably in successive shells of 2, 8, 8, 18, 18, 32 electrons.

The inert gases are characterised by the absence of their chemical reactivity. On the other hand, the elements which closely precede or follow the inert gases in the Table are found to be strongly chemically reactive. Those which precede, e.g., F, O, S, Cl, Br, etc., are electronegative and those which follow, e.g., Na, Mg, K, Ca etc., are electropositive. Because of the contrasting electrical character, the atoms of elements preceding an inert gas readily combines with those of elements following an inert gas; e.g., sodium spontaneously unites with chlorine. The valence of the elements is determined by the distance of the position of the element from the inert gas, e.g., 1 for sodium and for chlorine, 2 for oxygen and magnesium, 3 for aluminium and phosphorus, etc. The recurrence of the common characteristics in the different columns justifies the statement that properties of the elements are periodic functions of their atomic numbers.

The chemical activity of an atom depends upon the magnitude of its external electric field. The atoms of the inert gas elements not only show lack of chemical activity but also exhibit little tendency to form polyatomic molecules or to condense easily into liquids or solids. All the inert gases are monatomic and have very low boiling points. It may then be reasonably concluded that electronic arrangement in the inert gas atoms is such that these have very weak fields at the periphery. In other words, the arrangement of electrons in the atoms of inert gases must be such as to have especially low energy, *i.e.*, the most stable arrangement. The atom of an element which follows an inert gas in the Table has one or two electrons outside the stable inert gas core. These electrons are easily detachable yielding positive ions, *e.g.*, K-atom will lose an electron to form the stable argon core with a unit +ve charge. In fact, in the solid state these easily detachable electrons become somewhat loose as to render these elements good conductors of electricity.

On the other hand, the elements preceding inert gases, require one or two electrons to attain the inert gas core. That is why elements, like chlorine, preceding inert gases easily pick up electrons to produce negative ions. Since these elements have no extra electrons to spare to become loose, these are non-conductors. This scheme thus naturally explains the metallic and non-metallic characters of the elements.

The ready reaction between electropositive and electronegative elements is also clearly explained from this concept. In the formation of calcium chloride calcium readily parts with two extra electrons to form the stable argon structure, and two atoms of chlorine will pick up one electron each to form the stable argon structure. The two ions remain bound together now by electrostatic attraction to form the molecule of calcium chloride. In aqueous medium, however, the ions separate due to the weakening of the attraction. We thus see that the assumption of a stable structure for the inert gas atoms with low energy can explain the chemical and physical characters of the atoms.

To understand the significance of the classification then it is necessary to explain two broad facts : (1) why certain configurations are highly stable and (2) why systematic sequences occur in the periodic table between inert gases? It has also been seen that as the sequences become longer, the elements tend to become chemically similar as in rare earths or transitional elements.

Wave mechanics supplemented by the Pauli Principle furnishes the most satisfactory explanation of the periodic classification of elements. Starting with hydrogen ($Z = 1$), as we progress in the order of atomic numbers, the number of electrons in the atom must also increase by one with each step. The electronic configuration of the atoms is thus built up by successive addition of an electron to the preceding one in the Table. To obtain the most stable or ground state of an atom, the electron must be in the lowest possible energy-level, subject to Pauli's exclusion principle. As the atomic number increases, the electrons should gradually fill up shells and sub-shells systematically ; the quantum numbers of the electrons chosen are such as to place them in the most tightly bound state possible, reducing the potential energy of the atom to a minimum.

In the table below, are given the electronic configurations of the elements on the principle stated above and these are also supported from chemical and spectroscopic data.

The first element hydrogen ($Z = 1$) has only one electron. For the normal state of the atom, the electron should be in a $1s$ -electronic quantum state. The next element is He ($Z = 2$). The two electrons can both come into $1s$ -orbit, whereby the potential energy will be a minimum. The arrangement would be spherically symmetrical and there would be no residual field outside the atom. The configuration of helium is then $1s^2$, the K -shell is thus completely filled up.

With the next element lithium ($Z = 3$) an electron must occupy a position in the L -shell. Again for lowest possible energy level, two electrons of lithium shall be in K -shell and one electron in the $2s$ -orbit. That is, its configuration is $1s^2 2s$. Lithium thus should have a valency one, which is a fact. It is comparatively much easier to remove a $2s$ -electron than an $1s$ electron from this atom. That is

THE ARRANGEMENT OF ELECTRONS IN THE ATOMS OF THE ELEMENTS IN THEIR GROUND STATES

	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s	
1 H	1																		1s Full
2 He	2																		
3 Li	2	1																	2s Full
4 Be	2	2																	
5 B	2	2	1																
6 C	2	2	2																
7 N	2	2	3																
8 O	2	2	4																
9 F	2	2	5																
10 Ne	2	2	6																2p Full
11 Na	2	8		1															3s Full
12 Mg	2	8		2															
13 Al	2	8		2	1														
14 Si	2	8		2	2														
15 P	2	8		2	3														
16 S	2	8		2	4														
17 Cl	2	8		2	5														
18 A	2	8		2	6														3p Full
19 K	2	8		8			1												4s Full
20 Ca	2	8		8			2												
21 Sc	2	8		8	1		2												
22 Ti	2	8		8	2		2												
23 V	2	8		8	3		2												
24 Cr	2	8		8	5		1												
25 Mn	2	8		8	5		2												
26 Fe	2	8		8	6		2												
27 Co	2	8		8	7		2												
28 Ni	2	8		8	8		2												
29 Cu	2	8		8	10		1												
30 Zn	2	8		8	10		2												3d Full
31 Ga	2	8		18			2	1											
32 Ge	2	8		18			2	2											
33 As	2	8		18			2	3											
34 Se	2	8		18			2	4											
35 Br	2	8		18			2	5											
36 Kr	2	8		18			2	6											4p Full
37 Rb	2	8		18			8				1								5s Full
38 Sr	2	8		18			8				2								
39 Y	2	8		18			8	1			2								
40 Zr	2	8		18			8	2			2								
41 Nb	2	8		18			8	4			1								
42 Mo	2	8		18			8	5			1								
43 Tc	2	8		18			8	6			1								
44 Ru	2	8		18			8	7			1								
45 Rh	2	8		18			8	8			1								
46 Pd	2	8		18			8	10											
47 Ag	2	8		18			8	10			1								
48 Cd	2	8		18			8	10			2								4d Full
49 In	2	8		18			18				2	1							
50 Sn	2	8		18			18				2	2							

THE ARRANGEMENT OF ELECTRONS IN THE ATOMS OF THE ELEMENTS IN THEIR GROUND STATES

	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s	
51 Sb	2	8		18				18			2	3							
52 Te	2	8		18				18			2	4							
53 I	2	8		18				18			2	5							
54 Xe	2	8		18				18			2	6							
											5p Full								
55 Cs	2	8		18				18			8				1				
56 Ba	2	8		18				18			8				2				
57 La	2	8		18				18			8		1		2				
58 Ce	2	8		18				18			8				2				
59 Pr	2	8		18				18		2	8				2				
60 Nd	2	8		18				18		3	8				2				
61 Pm	2	8		18				18		4	8				2				
62 Sm	2	8		18				18		5	8				2				
63 Eu	2	8		18				18		6	8				2				
64 Gd	2	8		18				18		7	8				2				
65 Tb	2	8		18				18		7	8		1		2				
66 Dy	2	8		18				18		9	8				2				
67 Ho	2	8		18				18		10	8				2				
68 Er	2	8		18				18		11	8				2				
69 Tm	2	8		18				18		12	8				2				
70 Yb	2	8		18				18		13	8				2				
71 Lu	2	8		18				18		14	8				2				
								18		14	8		1		2				
72 Hf	2	8		18					32		8		2		2				
73 Ta	2	8		18					32		8		3		2				
74 W	2	8		18					32		8		4		2				
75 Re	2	8		18					32		8		5		2				
76 Os	2	8		18					32		8		6		2				
77 Ir	2	8		18					32		8		7		2				
78 Pt	2	8		18					32		8		8		2				
79 Au	2	8		18					32		8		9		1				
80 Hg	2	8		18					32		8		10		1				
									32		8		10		2				
81 Tl	2	8		18							5d Full								
82 Pb	2	8		18					32		18				2	1			
83 Bi	2	8		18					32		18				2	2			
84 Po	2	8		18					32		18				2	3			
85 At	2	8		18					32		18				2	4			
86 Rn	2	8		18					32		18				2	5			
									32		18				2	6			
											6p Full								
87 Fr	2	8		18					32		18								
88 Ra	2	8		18					32		18				8			1	
89 Ac	2	8		18					32		18				8			2	
90 Th	2	8		18					32		18				8			2	
91 Pa	2	8		18					32		18				8		1	2	
92 U	2	8		18					32		18		2		8		2	2	
93 Np	2	8		18					32		18		3		8		1	2	
94 Pu	2	8		18					32		18		5		8		1	2	
95 Am	2	8		18					32		18		6		8			2	
96 Cm	2	8		18					32		18		7		8			2	
97 Bk	2	8		18					32		18		7		8			2	
98 Cf	2	8		18					32		18		9		8		1	2	
99 En	2	8		18					32		18		10		8			2	
100 Fm	2	8		18					32		18		11		8			2	
101 Md	2	8		18					32		18		12		8			2	
102 No	2	8		18					32		18		13		8			2	
									32		18		14		8			2	
																		2	

Transition elements
(---Rare earths or lanthanons---)

Actinons

why first ionisation potential of lithium is 5.39 volts and 2nd ionisation potential is 75.6 volts.

Beryllium, the next atom in the Periodic Table ($Z = 4$) has two electrons in $1s$ and two in $2s$ orbit, having the configuration $1s^2 2s^2$. It is obvious that K -shell is completed and the s -subgroup of L -shell is also filled up. With boron ($Z = 5$), the added electron will have to occupy a place in the p -orbit of the L -shell as the other lower energy-levels are already filled up. The electronic configuration for boron is then $1s^2 2s^2 2p$. This process of gradual filling up of shells and subshells will continue until we reach the turning point at neon ($Z = 10$), when both K -shell and L -shell are completed with electrons. Neon is then $1s^2 2s^2 2p^6$.

The eleventh atom is sodium, immediately after the inert neon. Since K - and L -shells are fully occupied by ten electrons, the eleventh electron, for the minimum of potential energy, will take a place in M -shell at s -subgroup, *i.e.*, its configuration will be $1s^2 2s^2 2p^6 3s$. This process will continue until we reach argon ($Z = 18$), when K -shell, L -shell and s and p -subgroups of M -shell are completed (see the table above). It will be noticed that after the completion of each shell, a new period begins as is expected from chemical data. The completion of a shell or subshell means the most stable positions with weak external field and hence chemical inertness. The valency is really determined by the extent of incompleteness of the outermost shell.

The configuration of argon is $1s^2 2s^2 2p^6 3s^2 3p^6$. In the next element Potassium ($Z = 19$) we expect that the 19th electron (beyond the argon configuration) should take a position in $3d$ -state (*i.e.*, $n = 3$, $l = 2$). But potassium closely resembles lithium and sodium in its chemical characters and further, these produce identical spectra. These spectra are caused by the electrons at the periphery. It is therefore suggested that the 19th electron will occupy a place in the $4s$ -state than in $3d$ -state. Theoretical calculation later indicated that the potential energy in $4s$ -state in the atom is less than that in the $3d$ -state. The electronic structure of potassium should then be $1s^2 2s^2 2p^6 3s^2 3p^6 4s$.

In calcium ($Z = 20$) $3d$ -sublevel is not occupied but two electrons go to $4s$ -levels; Ca, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. After calcium, however, $3d$ -sublevel begins to be gradually completed until we come to zinc ($Z = 30$). Beyond zinc, since $4s$ -subgroup is already filled up, electrons successively add themselves to $4p$ -subgroup. On the completion of $4p$ -subgroup, we arrive at ($Z = 36$) krypton, having the configuration, $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$.

The table however indicates that the $3d$ -sublevel is already completed with Copper ($Z = 29$), the configuration shown is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$. This means that copper should behave like an alkali metal with one electron in $4s$ -orbital. But this is not so, the $3d$ -levels and $4s$ -levels are so close in Copper that bivalent Cu^{++} ions are readily formed.

The sequence of metals from Sc ($Z = 21$) to Cu ($Z = 29$) form the transitional elements. In these also $3d$ - and $4s$ -levels are quite close and that is why they are apt to show variable valence and coloured compounds.

The element following Kr is rubidium ($Z = 37$), which is a typical alkali metal and has a $5s$ -electron in spite of $4d$ - and $4f$ -levels remaining unfilled. Similarly, in the following element Sr we have two $5s$ -electrons and it behaves like calcium. From the next element Y ($Z = 39$) the $4d$ -levels are lower than $5p$, so commencing from element Y to element Ag ($Z = 47$) the $4d$ -levels are first filled up. These elements constitute the second transitional series.

Silver ($Z = 47$) has a configuration like that of copper and next element Cd like that of mercury. These two elements have $4d$ -levels completed and have 1 and 2 electrons in $5s$ -level.

The $5s$ - and $5p$ -orbitals are completed with xenon which is followed by the alkali metal Cs with one $6s$ -electron and Ba with two $6s$ -electrons.

In the next element lanthanum, the added electron, enters the $5d$ -level and a next transitional series is expected as with scandium earlier. But with the rise in atomic number, (Z) it was found that $4f$ -levels are now sufficiently low and this level is first filled up in preference to $5d$ -level. The maximum number of electrons that can be accommodated in $4f$ -level ($l = 3$) is $2(2l+1)$, *i.e.*, $2(2 \cdot 3 + 1) = 14$.

So 14 elements from Ce to Lu are obtained in which successively the $4f$ -levels are filled up. All these fourteen elements have outer configuration $5s^2 5p^6 6s^2$. This is why these 14 rare earth elements, as they are called, have identical chemical properties and their separation is so difficult.

Hafnium comes after the rare earth elements with ($Z = 72$), with the outer configuration $5d^2 6s^2$. After Hafnium, $5d$ -orbital is filled up producing another transitional series. Then begins the building up of the $6p$ -levels. This ends with Radon with an outer $6s^2 6p^6$ structure and hence inert in character. The same procedure continues after radon with the radioactive transuranic elements. Careful observation of the table would indicate that with Ac, $5f$ -shell begins to be filled instead of $6f$ -or $7p$ -levels. The result is, like lanthanide rare earths, a series of similarly behaving elements beginning from Ac ($Z = 89$) called Actinide rare earths.

Thus we see how a beautifully simple scheme explains the entire classification of the elements indicating the regular variation in their properties. We have thus gained a real insight into the structure of the atoms.

We may have an idea of the relative energy levels of p , d , f , orbitals with increased electronic charges from the diagrammatic representation given in Fig. V.35. This explains the preferential filling up of the sub-levels.

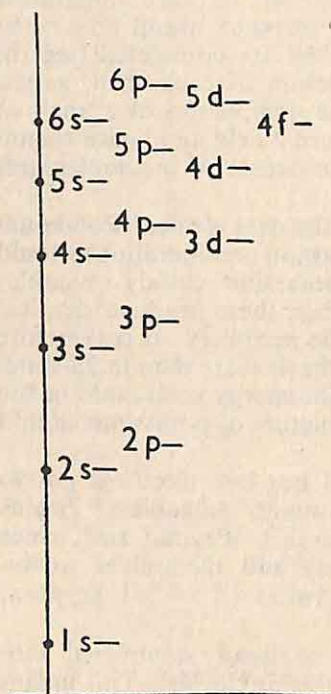
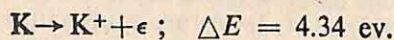


FIG. V.35 Energy levels of orbitals (diagrammatic)

V.31. Ionisation Potential and Electron Affinity. It is necessary to mention here two atomic quantities which have a bearing on the atomic structure and indicate the chemical character of the element to a large extent. These are the *ionisation potential* and the *electron affinity*.

The ease with which the outermost electrons, i.e., the valence electrons, can be removed is a guide to the ease with which the element forms positive ions and thus it is a guide to its chemical reactivity. The ionisation potential (I_0) is a measure of the energy required to remove a valence electron from a neutral atom in its ground state; it is expressed in e.v. units. We have seen in Sec V.19 an estimate of the ionisation potential of hydrogen. Naturally the weakest bound electron is removed first when we obtain the first ionisation potential;



$$(1 \text{ e.v.} \equiv 23.06 \text{ Kcals/gm-atom})$$

The first ionisation potentials of some atoms are given in the Table below :

Element	I_0 (e.v)	Element	I_0 (e.v)	Element	I_0 (e.v)
H	13.60	Li	5.39	Be	9.32
He	24.58	Na	5.12	Mg	7.64
Ne	21.56	K	4.34	Ca	6.11
A	15.76	Rb	4.18	Sr	5.7
Kr	14.0	Cs	3.90	Ba	5.20

The ionisation potential depends on three factors :

(i) the distance of the electron from the nucleus; since the attraction is electrostatic, ionisation potential will decrease with increase in R , the atomic radius. The I. P. decreases with increased size, e.g., in Group I metals.

(ii) the magnitude of the nuclear charge ;

(iii) the screening effectiveness of the other electrons on the nucleus.

Once the weakly bound outermost electron is removed, the other valence electrons are held more firmly from the centre with increased positive charge. It becomes progressively harder to remove the second and the third electrons. It is not surprising that second ionisation potential is often nearly double the first, when electrons are removed from the same shell. To illustrate :

	Be	C	N	F	Mg	Ca
1st ionisation potential	9.32	11.26	14.5	17.4	7.64	6.11
2nd ionisation potential	18.21	24.38	29.0	34.9	15.03	11.37

The energy given out when an electron adds to a neutral atom is known as the *electron affinity*. The electron affinities of the halogens of the VIIth group are the highest as these have only one electron short of an inert-gas structure. The electron affinities of metals are usually very low.

	Electron affinities						
Ion formed :	F ⁻	Cl ⁻	Br ⁻	I ⁻	O ⁻	S ⁻	O ⁻⁻ S ⁻⁻
Electron affinity (ev)	3.62	3.80	3.56	3.28	1.3	1.70	-7.28 -3.44

Addition of a second electron to a negatively charged ion becomes quite difficult in view of the electrostatic repulsion. Although O⁻⁻ and S⁻⁻ would have inert-gas configurations by addition of two electrons, yet the addition of the second electron requires so much energy that electron affinities become negative.

SUGGESTIONS FOR FURTHER READING

1. Quantum theory and Wave mechanics — Dushman, J. Chem Edn 8, 1074, 1931
2. The nature of the chemical bond — Pauling
3. Source book of atomic energy — Glasstone
4. Elementary wave mechanics — Heitler
5. Atomic spectra — Kuhn
6. Atomic spectra and Atomic structure — Herzberg
7. Quantum chemistry — Pitzer.

Problems

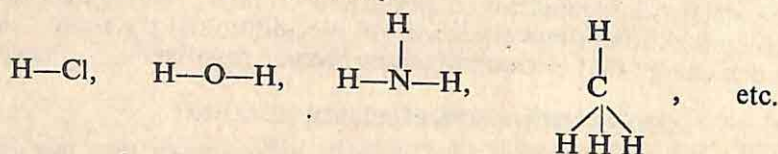
1. Calculate the wave numbers ($\bar{\nu}$) and wave lengths (λ) of the 1st line in the Lyman and the Balmer series.
2. Calculate Bohr's radius of the second orbit of the hydrogen atom.
3. Calculate the mass of an electron moving with a velocity 1×10^{10} cm sec⁻¹.
4. Find out the velocity of the electron in the first Bohr orbit of the hydrogen atom. Calculate also its kinetic energy and total energy.
5. What is the wavelength associated with a particle of mass 0.1 mg moving with a speed of 1×10^5 cm sec⁻¹ ?
6. What will be the wavelength of an electron when its kinetic energy is 1 ev? Calculate the wavelength of an electron accelerated through a potential difference of 1 Mev.
7. A worm (mass 0.1 gm) is moving with a velocity of 0.01 cm/sec. What is the uncertainty in its position?
8. (i) What do the following configurations represent :
 (a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$ (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
 (ii) Give the electronic arrangements of :
 (a) Li (b) Cr⁺⁺⁺ (c) I (at no. 53) (d) Ra (at no. 88).
9. Explain :
 (a) inertness of argon (b) variable valence of iron
 (c) similarity in chemical properties of rare-earth elements
 (d) chemical behaviour of Radium is like that of Barium.
10. Given

	mass
${}^1_1\text{H}$	1.007825
${}^1_0\text{n}$	1.008665
${}^4_2\text{He}$	4.002604

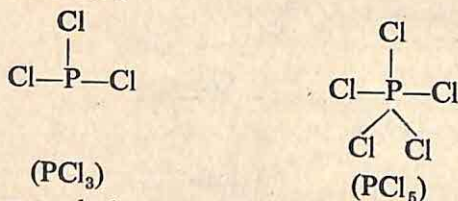
Show that the binding energy per nucleon in helium nucleus is 7.083 Mev.

THE CHEMICAL BONDING

VI.1. Historical. One of the fundamental questions of chemistry ever since the beginning of its study was to find out the nature of forces which bound atoms together to form molecules. The answer was not easy to find. After nearly a century of confusion, it was only in the latter part of the nineteenth century that a more or less qualitative concept of the mechanism of union of atoms crystallised out due to the contribution of a host of thinkers like Kekule, Van't Hoff, Le Bel, Werner and others. It was easily realised that the number of atoms of an element that would combine with an atom of another given element is not unlimited. Every element has a saturation capacity in respect of its union with another element. The saturation capacity or *valency* of an element, as it is usually called, is defined in a limited sense as the number of hydrogen (or chlorine) atoms with which one atom of the element can combine. Thus, chlorine, oxygen, nitrogen and carbon have valences 1, 2, 3 and 4 respectively,

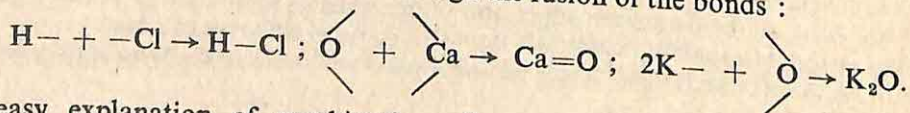


In many cases however, this number may vary, *i.e.*, some elements may have variable valence. To illustrate :

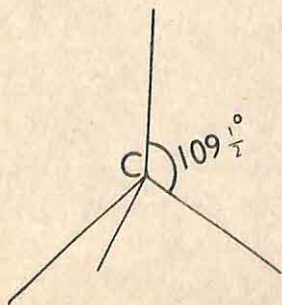


It is generally assumed that the valences were more or less like "bonds" associated with the atoms as depicted above. Thus, hydrogen, chlorine, sodium, are supposed to possess a single bond ; oxygen, calcium have two bonds ; nitrogen, bismuth have three bonds and so on.

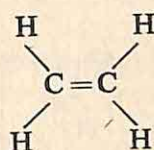
$\text{H}-, \text{Cl}-, \text{Na}-; -\text{O}-, -\text{Ca}-; -\text{N}-, -\text{Bi}-; \text{etc.}$
Each bond of an atom has the capacity of linking with one hydrogen or chlorine atom. The union of two atoms occur through the fusion of the bonds :



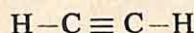
The easy explanation of combination of atoms through such bonds leads naturally to the view that there exist at some points in the atom directed forces represented by bonds. It means in the atom the valency forces are space-oriented, *i.e.*, the bonds have definite arrangement in space. This idea was developed by Van't Hoff and Le Bel independently and they suggested that carbon was quadrivalent and its four valences were directed towards the four corners of a regular tetrahedron, making an angle of approximately 109° between the bonds. This hypothesis of tetrahedral model of carbon had an outstanding achievement when it clearly explained not only the optical activity of organic compounds,



the existence of isomers, but also the structure of other saturated molecules. Excepting in CO, in all other carbon-compounds, carbon was considered quadrivalent and was given the tetrahedral model. To retain the quadrivalency of carbon, it was however necessary to assume the formation of double and triple bonds between carbon atoms in unsaturated compounds, as in ethylene or acetylene.

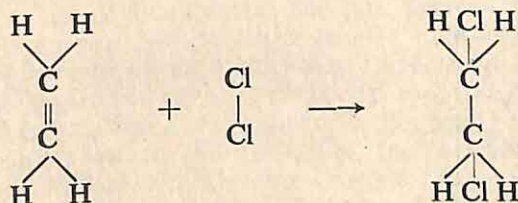


ethylene

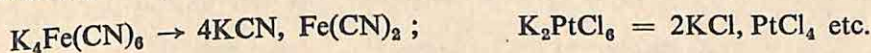


acetylene

Such unsaturated compounds are highly reactive as they possess a spontaneous tendency to be saturated. Saturated molecules are those in which all C-C linkages are single-bonded. This is why unsaturated compounds easily form additive compounds by releasing its valences from double and triple bonds to unite with available atoms or groups.

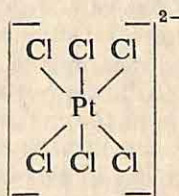
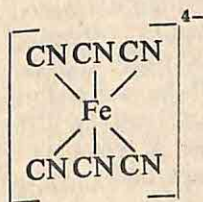


The theory of valence bonds enunciated so far was not found sufficient to elucidate the formation of various complex salts, soluble salts and hydrates, such as cuprammonium compounds, platinichlorides, ferrocyanides, etc. These compounds may be represented as two compounds united together, such as,



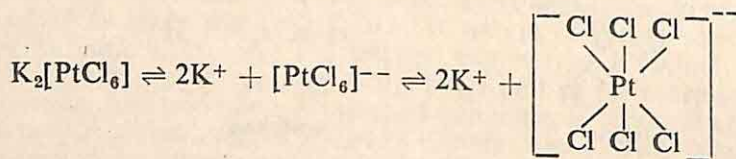
But such representation would not be correct in view of the fact that the separate existence of the two molecules is not revealed in the formation of their ions in solution. Potassium ferrocyanide solution yields $\text{Fe}(\text{CN})_6^{4-}$ ions instead of Fe^{2+} ions. Similarly chloroplatinic acid contains PtCl_6^{2-} ions, and cuprammonium salts produce $\text{Cu}(\text{NH}_3)_4^{2+}$ ions.

It is evident that six (CN) radicals are linked to the iron atom in ferrocyanides, six Cl-atoms are associated with the Pt-atom in platinichlorides. Their structures are expressed in the form :

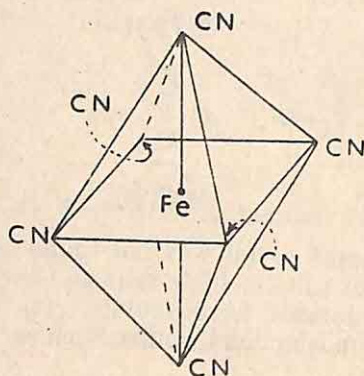


It appears the central atoms "Fe" and "Pt" exhibit a maximum valency of six. To explain the formation of such complex molecules, Werner (1891) proposed a new theory, which was subsequently found to be quite correct. According to this theory, certain atoms have a capacity to link to themselves a definite number of other atoms or radicals (or even molecules) irrespective of their own valency. These groups or radicals are rather firmly attached to the atom, called central atom, and do not ionise. The maximum number of the groups or radicals attached to the central atom is usually six (or four) and is called the *co-ordination number*. The atoms or groups thus attached to the central atom constitute the inner zone of the complex molecule. In the outer zone, also, the molecule may contain other

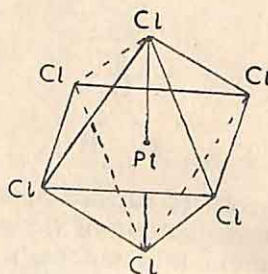
atoms or radicals, which are not held very firmly and may ionise. To take the example of potassium chloroplatinate, K_2PtCl_6 , the co-ordination number of the central Pt-atom is six; six chlorine atoms are attached to the Pt-atom forming the $(PtCl_6)^{2-}$ co-ordinated complex, in which the chlorine atoms would not ionise being in the inner zone. In the outer zone are attached two potassium atoms which ionise easily. It is obvious the complex ion is a divalent one.



The atoms or radicals in the co-ordinated complex have also a definite spatial arrangement. The six-co-ordinated complexes possess octahedral structures.



(a) $[Fe(CN)_6]^{4-}$



(b) $[PtCl_6]^{2-}$

Werner's theory was supported from the chemical behaviour shown by the co-ordinated compounds and was also established from the structural isomerism exhibited by such compounds, wherever possible. In the beginning, this idea of a central atom taking up six coordination groups irrespective of its own valency had a poor acceptance but subsequent knowledge proved the theory to be essentially sound.

These ideas about valency, developed by the chemists based on factual observation of the chemical behaviour of the molecules, preceded the Rutherford-Bohr work on the concept of atomic structure. But the developments on the theory of valency at the time were not made with an understanding of the nature of forces which caused the different types of union between atoms or the arrangement of atoms in the molecule. The knowledge of electronic configuration of atoms in the beginning of this century gave a new and reasonable interpretation of bonding between atoms and an understanding of the affinities exerted by atoms in their union. This is often mentioned as the electronic theory of valency.

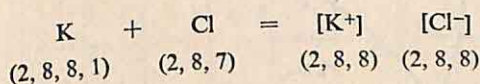
We have seen in the previous chapter that the extraordinary stability of inert gases is due to their stable electronic configuration; all the inert gases have eight electrons in their outermost orbit. The elements which immediately precede an inert gas in the periodic table, namely the halogens, are all strongly electronegative and univalent. The elements which immediately follow the inert gases in the table, *i.e.*, the alkali metals, are all strongly electropositive and univalent. It was suggested that the atoms of different elements would always try to acquire a stable configuration of eight electrons in their outermost shell, akin to that of the inert gases.

This is the fundamental principle of the electronic theory of valency. The achievement, of stable configuration is possible mainly in two ways. Basically there are two extreme cases of chemical bonding and compounds are characterised either by one or the other and in many cases by an admixture of the two. These two extreme nature of bonding should therefore be treated separately.

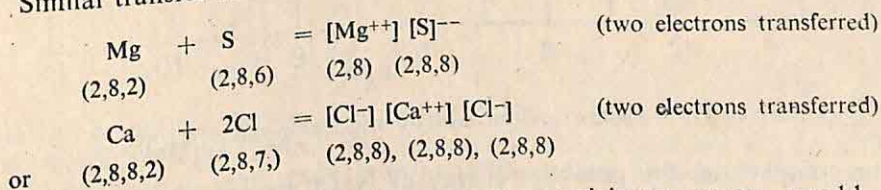
VI.2. The Ionic Bond. The atomic structures of halogens and alkali metals vis-a-vis the inert gases are :

<i>Halogens</i>	<i>Inert gases</i>	<i>Alkali metals</i>
F (2, 7)	Ne (2, 8)	Na (2, 8, 1)
Cl (2, 8, 7)	Ar (2, 8, 8)	K (2, 8, 8, 1)
Br (2, 8, 18, 7)	Kr (2, 8, 18, 8)	Rb (2, 8, 18, 8, 1)
I (2, 8, 18, 18, 7)	Xe (2, 8, 18, 18, 8)	Cs (2, 8, 18, 18, 8, 1)

Every halogen atom has seven electrons in its outermost orbit and would need only one electron to attain the stable configuration of the nearest inert gas. On the other hand, every alkali metal has one electron in the outermost orbit which it would try to part with in order to attain for itself a stable configuration. Kossel (1916) developed the theory that in the formation of molecules like KCl, which readily ionise and conduct electricity in solutions a transfer of electron occurs from one atom to another producing stable configurations. Thus, when a potassium atom unites with a chlorine atom, the former readily parts with its outermost electron and the latter takes up the same. The potassium atom becomes positively charged K^+ ion with a stable structure, while the chlorine atom is rendered into negatively charged Cl^- ion also with a stable structure. The two oppositely charged ions remain associated together by electrostatic forces to constitute the molecule. It means that in the formation of KCl molecule transfer of electron takes place from one atom to the other. The ions would separate from one another under suitable conditions, say, in a solution.



Similar transfer of electrons also occurs in other compounds, e.g.,



It is evident in such combinations, every participant atom would attain the stable inert gas configuration. Such a chemical bond with transfer of electron has been named *ionic bond* and the resultant molecules are ionic compounds.

That in a molecule formed through ionic bond the two oppositely charged ions exist together through coulombic attraction can be easily understood from energy consideration. Let us consider the case of NaCl molecule. In chapter III, we have seen that the solid crystal of sodium chloride consists of definite arrangement of Na^+ and Cl^- ions and to speak of sodium chloride molecule is meaningless. The existence of a molecule of sodium chloride can be visualised only in the vapour phase. It is presumed that a Na^+ ion and a Cl^- ion are bound there through electrostatic attraction. Both the ions carry unit charge, e . If r be the internuclear separation, then the attractive potential energy of the system is $e(-e)/r = -e^2/r$. When the two ions are sufficiently close, there shall also be a repulsion between the two nuclei or between the inner-shell electrons. Born and Meyer suggested empirically that this repulsion potential may be expressed in the

form be^{-ar} , where 'a' and 'b' are constants. In all ionic bonds, 'a' is taken to be approximately equal to $3.3 \times 10^8 \text{ cm}^{-1}$. The net potential energy of the system $[\text{Na}^+][\text{Cl}^-]$ is

$$U = -\frac{e^2}{r} + be^{-3.3 \times 10^8 r} \quad \dots (VI.1)$$

Using the experimental value of 'r' as the equilibrium internuclear distance where the pot. energy is at its minimum, a numerical value may be assigned to 'b'. Since a and b are now known, the potential energy (U) can be calculated for different values of the distance r from eqn (VI.1) and can be plotted graphically as in Fig. VI.2. The U-r graph plotted with experimental data from spectroscopic measurements coincides with the one derived theoretically at relatively short nuclear separations. This confirms the co-existence of Na^+ and Cl^- ions in the molecule, when the internuclear distance is small. With increase in r, the pot. energy tends to zero.

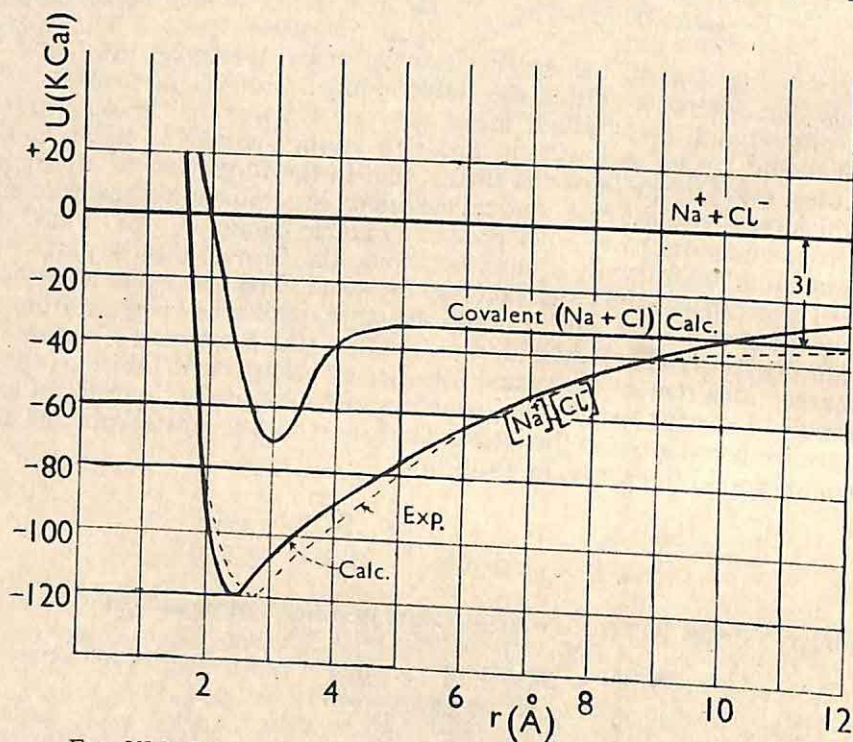


FIG. VI.2. Pot-energy variation with internuclear distance (NaCl).

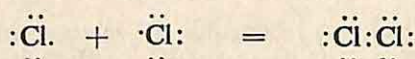
For comparison, the potential energy of NaCl assuming non-ionic linkage (say covalent union) was also calculated and plotted in Fig. VI.2. It shows that when the internuclear separation is relatively high, the pot. energy of (Na+Cl-) is less than that of (Na+Cl-). For,

Na	= Na ⁺ + e	ΔH(Kcals)
Cl + e	= Cl ⁻	118
Na + Cl	= Na ⁺ + Cl ⁻	-86
		32

That is, at relatively large separations, atomic (Na and Cl) are more stable than (Na⁺+Cl⁻), and the molecule should break up into atoms. Only at small distances, ($r < 10\text{Å}$) should these remain as ionic species constituting the molecule.

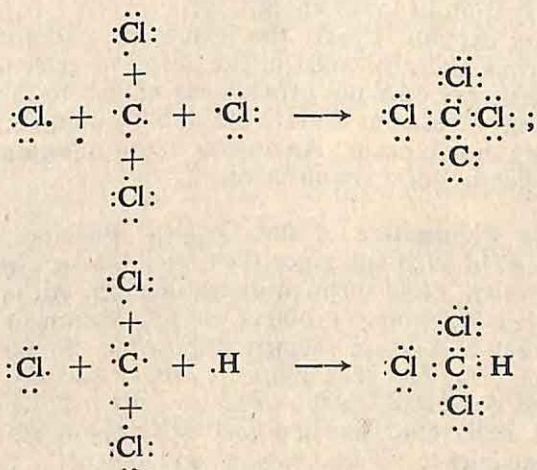
The ionic bond explains the formation of various salts, acids etc. which readily ionise, but it cannot account for the formation of molecules like H_2 , CH_4 , etc. For these compounds, the other type of bonding, namely the covalent bonding, has been proposed.

VI.3. The Covalent Bond. It was G. N. Lewis who pointed out first that it was possible for atoms forming a molecule to attain inert gas structure even without any transference of electron from one to the other. Lewis (1916) proposed that the union of atoms in molecules like H_2 , Cl_2 etc. and in most organic molecules, resulted from *sharing of a pair of electrons* between atoms in such a way as to give complete octets for the participating atoms. For example : a chlorine atom has seven electrons in the outermost shell. When two atoms unite to form a molecule of Cl_2 , each atom would contribute an electron to make a pair to be shared by both the atoms ;

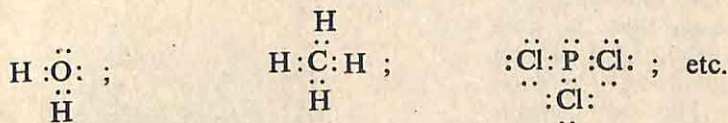


There is thus a common pair of electrons, supposed to belong to both the atoms, which counts in completing the octet round each atom. The central pair of electrons links the two atoms. This type of linking between two atoms by joint sharing of two electrons, one contributed by each participant, was named *covalency* (or *covalent bonding*) by Langmuir.

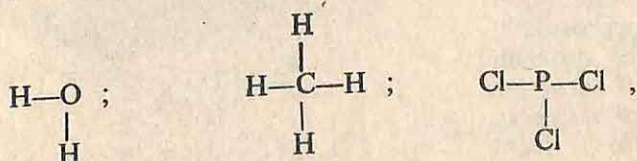
We can cite other examples. Carbon has four electrons in the outermost shell and it needs four electrons to complete the octet. These four may be obtained by common sharing of electrons with four chlorine atoms, or (say) three chlorine and one hydrogen atom, as follows :



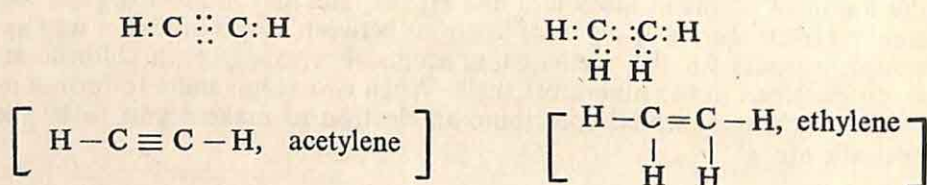
It will be noticed that each atom has attained stable inert gas configuration. In the case of hydrogen, instead of an octet, a duplet of electrons will be sufficient to produce nearest inert gas (Helium) configuration. Similarly, the formations of methane, water, phosphorus trichloride take place through covalent bonding, as :



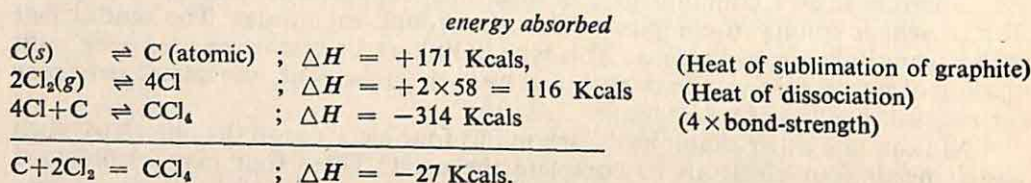
Ordinarily, the valence bond is represented by a line between atoms, as



Each covalent bond is thus equivalent to a pair of electrons. In unsaturated compounds, it may be necessary for two atoms to share jointly more than one pair of electrons, as in ethylene, acetylene etc.



As with ionic bond, we may consider the energy changes in the formation of a covalent bond to find out its stability. In the case of CCl_4 formed from carbon and chlorine atoms, we may calculate as :



The formation of covalent bonds in the molecule is thus naturally expected to ensure stability from its lower energy-level.

Lewis theory explains clearly the formation of the covalent bond through sharing of electrons and also most of the chemical behaviour of covalent compounds. But the theory does not provide any answer to the fundamental question of how the sharing of electrons leads to the stability of molecules, or for that matter, why at all sharing should occur. An answer to this question ultimately was obtained from the application of wave mechanics.

VI.4. Qualitative Explanation of the Covalent Bonding. The Schrödinger wave equation appeared in 1926 and since then attempts were made to understand the nature of the covalent bond through its application. Although the wave equation successfully solved the atomic problem, its application to molecules led to such complications that a solution seemed impossible. So far only the simplest of molecules, namely H_2 , has been more or less adequately treated and even then the mathematical complexity is too great and beyond the scope of this text. We shall only try to understand here in a qualitative manner the results of the application of wave mechanics to the H_2 -problem, and in general, to the covalent bondings in other molecular systems.

In a hydrogen molecule, two atoms are linked together by a non-ionic or covalent bond, H-H. The system consists of two protons and two electrons. It is known that the two nuclei containing a proton each oscillate against each other. The equilibrium internuclear distance (r_e) and also the minimum energy at that separation have been experimentally determined. The problem is now to see if these experimental values of energy could be confirmed from

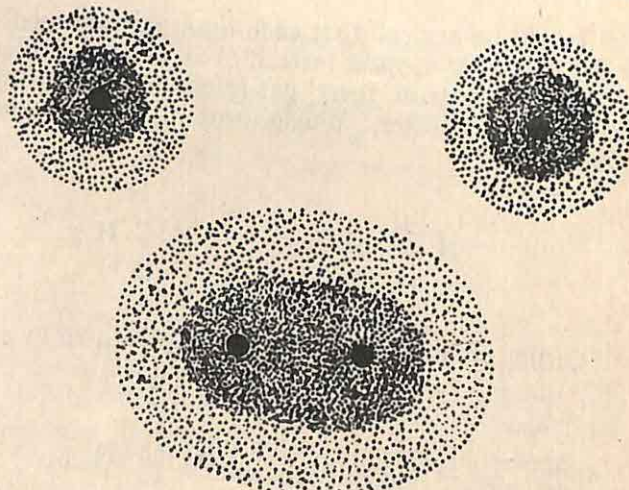


FIG. VI. 3

wavemechanical calculations. In such considerations, the wave properties of the electrons are to be analysed. When two H atoms, each with an electron in $1s$ orbital, approach each other, the electron waves overlap. In the overlapping, the two waves may be in opposition leading to destructive interference, called *anti-symmetric* mode of coupling. The result is an increase in the repulsive force so that no stable H_2 -molecule would be possible. On the other hand, when the electron waves overlap in such a way as to cause constructive interference, called *symmetric mode* of coupling, the electron density (proportional to ψ^2) in the region between the nuclei increases. This higher electron density, negative in character, really "cements" the two protons of the two nuclei (Fig. VI.3). The result is a stable H_2 -molecule. This is the explanation of the covalent bonding from wave properties. The excess electron density in the vicinity of the nuclei lowers the potential energy level. It is necessary now to evaluate mathematically the energy which, as already stated, is quite difficult. The quantum mechanical approach has been made in two ways; namely, (i) by valence-bond method and (ii) by molecular orbital method.

The Variational Principle. Before we proceed to discuss the approaches of the valence-bond and the molecular orbital theory for covalent bonding some general aspects of Ritz's variational principles used for approximate solution of Schrödinger equation need consideration.

Quantamechanically speaking, a knowledge of the wave function of a system, obtainable as the solution of Schrödinger equation, provides the basis for ascertaining the properties, including energy, of the system in the best possible way. Unfortunately, all molecular systems have their Schrödinger equations cast in forms that are not exactly soluble; even the simplest H_2 -molecule is no exception. It is therefore necessary to rely upon approximate methods of solution and consequently approximate wave functions ψ , which may then be further refined.

When applied to a molecular system, Ritz's variation principle concerns itself mainly with the evaluation of approximate value of energy and wave function in the ground state.

Since for the molecular system of interest exact wave-function cannot be obtained, an intuitive clever guess for the possible form of ψ is made. This approximate ψ may be very close to true ψ if the guess is a good one, or it may be far from true ψ if poor guess is made initially. The molecular property, say energy, can be evaluated with the assumed ψ . If the agreement with the experimental value is poor, the form of assumed ψ is modified. The process of iteration is continued until we close upon almost the true ψ and almost the true energy. In practice, an alternative procedure is often followed as indicated below.

Suppose the guess is $\psi = c_1\phi_1 + c_2\phi_2$ where the functional forms of ϕ_1 and ϕ_2 are known and c_1, c_2 , unknown initially, are independent of the variables. The wave equation will be

$$\nabla^2\psi + \frac{8\pi^2m}{h^2}(\epsilon - U)\psi = 0.$$

$$\text{or} \quad \epsilon\psi = \left[\frac{-h^2}{8\pi^2m}\nabla^2 + U \right] \psi$$

$$\text{or} \quad \epsilon\psi = H\psi$$

$$\text{where } H, \text{ the Hamiltonian operator is } \left[- \left(\frac{h^2}{8\pi^2m} \right) \nabla^2 + U \right].$$

$$\text{Hence.} \quad H(c_1\phi_1 + c_2\phi_2) = \epsilon(c_1\phi_1 + c_2\phi_2) \quad \dots (i)$$

Now according to a fundamental postulate of wave mechanics, the energy of the system, defined by ψ , is given as

$$\epsilon = \frac{\int \psi H \psi d\tau}{\int \psi^2 d\tau} \quad \dots (ii)$$

where $d\tau$ is a small element of volume in the configuration space and the integrals are to extend over the entire configuration.

From (i) & (ii), we have

$$\epsilon = \frac{\int [c_1\phi_1 + c_2\phi_2] H (c_1\phi_1 + c_2\phi_2) d\tau}{\int [c_1\phi_1 + c_2\phi_2]^2 d\tau} \quad \dots (iii)$$

or
$$\epsilon = \frac{c_1^2 A_{11} + c_2^2 A_{22} + 2c_1 c_2 A_{12}}{c_1^2 s_{11} + c_2^2 s_{22} + 2c_1 c_2 s_{12}} \quad \dots (iv)$$

where $A_{11} = \int \phi_1 H \phi_1 d\tau$; $A_{22} = \int \phi_2 H \phi_2 d\tau$; $A_{12} = \int \phi_1 H \phi_2 d\tau = \int \phi_2 H \phi_1 d\tau^*$

$$s_{11} = \int \phi_1^2 d\tau; \quad s_{22} = \int \phi_2^2 d\tau; \quad s_{12} = \int \phi_1 \phi_2 d\tau.$$

It will be remembered that c_1 and c_2 are unknown and for different magnitudes of the pair, the energy value (ϵ) will alter. In the ground state, the energy level will be minimum and such values are to be ascribed to c_1, c_2 as will make ϵ the lowest possible. This will be attained by the simultaneous satisfaction of the differential conditions,

$$\frac{\partial \epsilon}{\partial c_1} = 0 \quad \text{and} \quad \frac{\partial \epsilon}{\partial c_2} = 0.$$

Evaluating $\frac{\partial \epsilon}{\partial c_1}$ and $\frac{\partial \epsilon}{\partial c_2}$ from (iv) and equating each to zero, the following pair of relations emerge,

$$c_1[A_{11} - \epsilon s_{11}] + c_2[A_{12} - \epsilon s_{12}] = 0$$

$$c_1[A_{12} - \epsilon s_{12}] + c_2[A_{22} - \epsilon s_{22}] = 0$$

These two equations together with (ii) provide necessary requirements for evaluation of c_1, c_2 and ϵ . If the energy value only is required and not the wave function (which involves c_1 and c_2), the two simultaneous equations lead to the secular determinant, viz.,

$$\begin{vmatrix} A_{11} - \epsilon s_{11} & A_{12} - \epsilon s_{12} \\ A_{12} - \epsilon s_{12} & A_{22} - \epsilon s_{22} \end{vmatrix} = 0$$

from which ϵ can be easily determined. This method of minimisation of energy is one technique of treating atomic molecular problems wave-mechanically. Any successful application of this method depends on a clever assumption about the wave function in the first place and secondly on the mathematical feasibility of evaluating the integrals occurring in the above determinant.

The Valence-Bond Method. This approach for the interpretation of covalent bond originated in the works of Heitler and London (1927) just one year after Schrödinger's formulation of his famous wave equation. The method was further developed by Pauling and Slater. The contents of this method will be revealed through the specific illustration of the hydrogen molecule.

Let the two nuclei in the H_2 -molecule be represented by 'a' and 'b' and the two electrons labelled (1) and (2). If we start with two hydrogen atoms far from each other, their respective wave functions would be $\phi_a^{(1)}$ and $\phi_b^{(2)}$, the same as the H-atom wave functions in the ground state.

$$\left[\phi_a^{(1)} = \phi_b^{(2)} = \frac{1}{\sqrt{\pi}} e^{-R}, \text{ where } R \text{ is distance of the electron from the nucleus in Bohr units} \right]$$

*The two integrals are equal [See Margenau and Murphy, Mathematics of physics and chemistry (Van Nostrand, 1943), pp. 328].

Their separate energies are $\epsilon_a = \epsilon_b = \epsilon_H$ and their Hamiltonian operators viz. $\left[-\frac{h^2}{8\pi^2m} \nabla_1^2 + U_1 \right]$ and $\left[-\frac{h^2}{8\pi^2m} \nabla_2^2 + U_2 \right]$, which are independent

of each other, depend on the electronic co-ordinates of (1) and of (2) respectively. If we consider the two atoms far apart as forming one system of which the net wave function is ψ' and the energy $\epsilon_a + \epsilon_b = 2\epsilon_H$, it follows readily that $\psi' = \phi_a^{(1)} \phi_b^{(2)}$.^{*} If now the two atoms be moved towards each other, gradually their charge clouds and hence their orbitals or wave functions will start overlapping, necessitating gradual and simultaneous slow changes in orbitals $\phi_a^{(1)}, \phi_b^{(2)}$. The separate hamiltonians will no longer be independent and will give rise to a resultant hamiltonian, dependent on the co-ordinates of both the electrons and both the nuclei. Under such conditions, it is supposed that the wave function of the entire system is given by $\psi_1 = c_1 \phi_a^{(1)} \phi_b^{(2)}$, an expression similar to ψ' , which is in reality a guess-work. But Heitler and London pointed out the inadequacy of such an assumed orbital. There is hardly any experimental possibility of distinguishing the two electrons (1) and (2) when overlap occurs. It is also not possible to restrict an electron on to one nucleus. Hence the wave function $\psi_2 = c_2 \phi_a^{(2)} \phi_b^{(1)}$ is as much acceptable as ψ_1 . In sum Heitler and London guessed a wave function of H_2 -molecule which is a combination of ψ_1 and ψ_2 , viz.

$$\psi = \psi_1 + \psi_2 = c_1 \phi_a^{(1)} \phi_b^{(2)} + c_2 \phi_a^{(2)} \phi_b^{(1)}$$

The application of variational principles for the minimisation of energy of a system represented by this ψ evaluates c_1, c_2 and energy ϵ . For different fixed nuclear distances, calculations of such minimum energy values lead to the molecular energy diagram. From this diagram, the minimum energy of H_2 -molecule is found to be 3.14 e.v. for an internuclear distance of 0.869 Å, as against the experimental value of 4.74 e.v. for an equilibrium nuclear separation of 0.74 Å. Further refinements in the assumption of the trial wave-function ψ —incorporating polarisation, ionic contribution to bond etc. when overlap takes place—lead to the theoretical values of binding energy and equilibrium distance quite close to the observed ones, indicating the inherent correctness of approach of the valency bond theory in interpreting covalent link.

The essence of valence bond approach is thus to choose wave functions of two suitable electrons in the combining atoms and to form a joint orbital or space wave function.

$$\psi = c_1 \phi_a^{(1)} \phi_b^{(2)} + c_2 \phi_b^{(1)} \phi_a^{(2)}$$

with a minimum of energy. The description of two electrons in the molecule by a common space wave function requires separate spin characteristics (spin wave-functions) for two electrons, so that the resultant orbital (i.e., product of space and spin wave functions) becomes antisymmetric.

This is the quanta-mechanical interpretation of the Lewis original idea of electron pairing in covalent bond formation in H_2 molecule.

^{*}In such an assumption,

$$\begin{aligned} H\psi' &= \left\{ \left[-\frac{h^2}{8\pi^2m} \nabla_1^2 + U_1 \right] + \left[-\frac{h^2}{8\pi^2m} \nabla_2^2 + U_2 \right] \right\} \left(\phi_a^{(1)} \times \phi_b^{(2)} \right) \\ &= \phi_b^{(2)} \left[-\frac{h^2}{8\pi^2m} \nabla_1^2 + U_1 \right] \phi_a^{(1)} + \phi_a^{(1)} \left[-\frac{h^2}{8\pi^2m} \nabla_2^2 + U_2 \right] \phi_b^{(2)} \end{aligned}$$

$$\text{or } H\psi' = H \left(\phi_a^{(1)} \phi_b^{(2)} \right) = \phi_b^{(2)} \epsilon_a \phi_a^{(1)} + \phi_a^{(1)} \epsilon_b \phi_b^{(2)} = (\epsilon_a + \epsilon_b) \phi_a^{(1)} \phi_b^{(2)} = 2\epsilon_H \psi'$$

This conforms to reality when atoms are far apart. Hence the assumption $\psi' = \phi_a^{(1)} \phi_b^{(2)}$

The Molecular Orbital method. The m.o. method was originally developed by Mulliken, Hund and Lennard Jones and latterly perfected by a host of other workers. Here the starting point is the molecule or rather the skeleton of a molecule with its nuclei in fixed positions and the inner shell electrons occupying their non-bonding orbitals which are mostly the same as would be found in the separate atoms. The problem here is to ascribe wave functions or molecular orbitals to the original valence shell electrons of the atoms, when these bind the latter together into a molecule. In other words, just as atoms are built up by allowing electrons to occupy different atomic orbitals, molecules are likewise thought to be formed by electrons characterised by different wave functions or molecular orbitals distributed around a polynuclear framework.

The bare outlines of the principal features of this method will be explained in the context of bond formation in H_2 -molecule. The Hamiltonian operator for the hydrogen molecule consisting of two nuclei and two electrons is, (see Fig. VI.4),

$$H = -\frac{h^2}{8\pi^2m} [\nabla_1^2 + \nabla_2^2] + \frac{e^2}{R} - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} + \frac{e^2}{r_{12}}.$$

When ψ represents the molecular orbital, $H\psi = \epsilon\psi$. We should set out to find this approximate ψ in such a way that it (i) minimises energy and (ii) satisfies the Pauli exclusion principle when electronic spin wave functions are considered additionally.

In the first place we guess a trial wave function using our intuition or experience. One guess, proved useful, is to assume ψ to be constructed from one electron molecular orbitals each of which may be a *linear combination of known atomic orbitals* (L. C. A. O.). On this idea, electron (1) will tend to occupy a molecular orbital

$\psi_1 = c_1\phi_a^{(1)} + c_2\phi_b^{(1)}$ in the net electric field provided by the two nuclei and electron (2). Similarly, electron (2) will tend to occupy an orbital $\psi_2 = c_1\phi_a^{(2)} + c_2\phi_b^{(2)}$. This is simply a linear combination of two atomic hydrogen 1s-orbitals. The joint wave function or net molecular orbital ψ is then

$$\psi = \psi_1 \times \psi_2 = [c_1\phi_a^{(1)} + c_2\phi_b^{(1)}] [c_1\phi_a^{(2)} + c_2\phi_b^{(2)}]$$

Application of Ritz's method for the minimisation of energy with this trial wave function leads to values of c_1 , c_2 and ϵ . In actual evaluation, it turns out $|c_1| = |c_2|$, as is expected on symmetry grounds, and that two orbitals, corresponding to two energy values (one higher and one lower), result. It is the lower energy

value that only roughly agrees with the experimental value of the binding energy of the H_2 -molecule. Of the two orbitals, the one with the lower energy-value is called the bonding orbital and the other, the antibonding orbital. In the bonding m.o. the electrons have their charge distribution somewhat concentrated in between the two nuclei and also about the nuclei. In the antibonding orbital, the charges are pushed apart from each other.

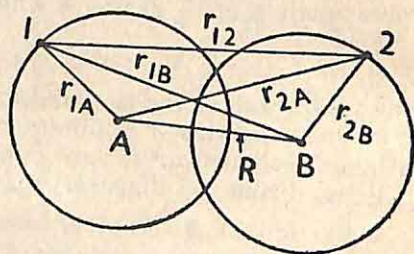


FIG. VI.4

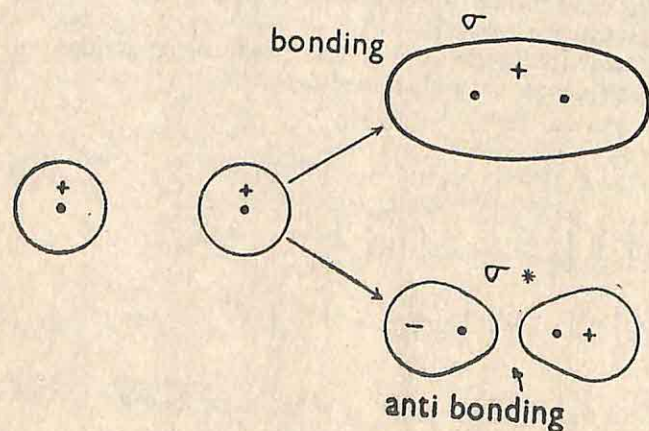


FIG. VI.5

It is a general mathematical result that the number of molecular orbitals is equal to the number of atomic orbitals used in the linear combination for the formation of m.o. The m.o.'s so obtained are made to occupy from the lowest energy upwards by electrons, two at the most per m.o. The spin wave functions of the pair of electrons should be such that the Pauli Principle is not violated.

The atomic orbitals chosen for linear combination to form molecular orbitals satisfy the characteristics :

- (i) Energies associated with the different atomic orbitals should not differ much.
- (ii) Symmetries of orbitals chosen should permit proper overlapping.
- (iii) Extent of overlap should be the maximum possible.

This is M.O. method. Both V.B. and M.O. methods are approximations used in applying Schrödinger equation to molecular systems.

VI.5. Directed Valence : Hybridisation. In the H_2 -molecule, for the formation of the molecular orbital, two $1s$ -atomic orbitals are involved. The s -orbitals being spherical the effect is the same from whichever direction the overlapping of the orbitals might have occurred. In s -orbital overlapping, there is no problem of directional orientation. But directional considerations become quite important when electrons in the p or d -orbitals take part in bond formation, as in chlorine, oxygen etc. The p -orbitals may overlap 'end on' as in Fig. VI.6(a) and give rise to a bond similar to that formed between s -orbitals. Such a bond is called a σ -bond. But the p -orbitals may also overlap 'sideways' as in Fig. VI.6(b), to give rise to a bond called π -bond. A double bond consists of two bonds, one σ -bond for p_x -orbitals (say) and another π -bond from p_z orbitals.

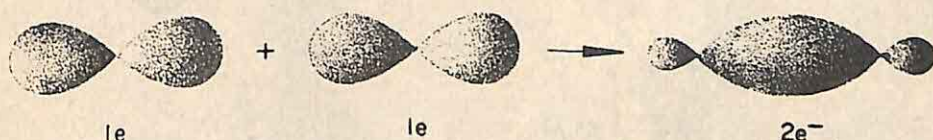


FIG. VI.6a σ -bonding orbitals

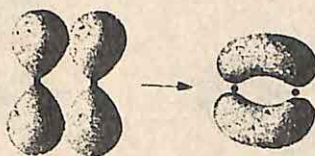
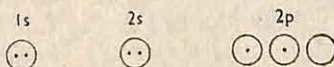


FIG. VI.6b π -bonding orbitals

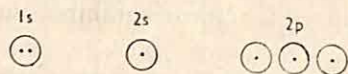
There is another important aspect in the directional consideration of bonding which needs mention here. Sometimes, two or more atomic orbitals may combine to yield an equal number of new atomic orbitals which are identical with one another but different from the original ones. This is also justified mathematically. For example, one s -orbital and three p -orbitals may combine to give rise to four identical sp^3 -atomic orbitals. This is called *hybridisation* and the new orbitals are *hybrid orbitals*. We may explain this with an illustration, say the bondings in methane.

In the ground state of a carbon atom, the electronic structure is $1s^2 2s^2 2p^2$. It has two unpaired electrons in the p -orbitals. This can be represented as



Normally it is expected that the two unpaired electrons will form two bonds

with the electrons of the combining element and carbon should exhibit a tendency to form two bonds. But four bonds do occur. It has however been found that with a small energy one of the $2s$ electrons may be excited to fill up the empty p -orbital, so that the structure becomes,



The carbon atom has now four unpaired electrons capable of entertaining four bonds, as in methane, combining with four electrons of four hydrogen atoms.

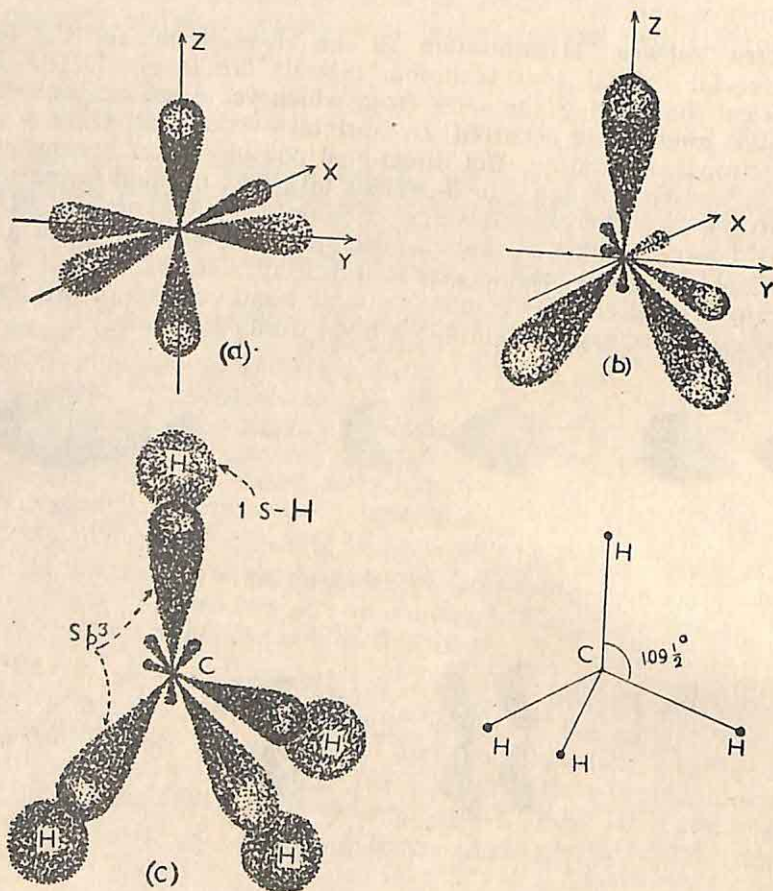


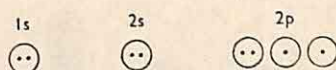
FIG. VI.7. (a) p_x , p_y , p_z orbitals (b) sp^3 hybrid orbitals
(c) sp^3 hybrids bonding with $1s$ -Hydrogen orbitals

The energy required for this initial excitation is more than compensated by the effective decrease in overall energy due to the formation of the two more extra bondings. We may next turn our attention to the orientation of these four bonds.

Of the four wave functions of carbon which would take part in bonding, one is associated with $2s$ -orbitals and the other three with $2p$ -orbitals. When these will couple with $1s$ -electrons of the four hydrogen atoms, we would expect one of the bonds different from the other three. But there is undisputed chemical evidence to establish the complete identity of the four bonds in methane and the molecule possesses a high degree of symmetry. In fact, the one $2s$ -orbital and the three $2p$ -orbitals combine and hybridise to form four new identical sp^3 -hybrid orbitals. These four hybrid orbitals are spatially oriented from the carbon

nucleus towards the four corners of a regular tetrahedron. The hybrid tetrahedral orbitals are quite stable and recede as far away as possible from one another, making an angle of $109^{\circ}28'$. These hybrid orbitals then couple with $1s$ -orbitals of the hydrogen atoms (Fig. VI.7). We thus see a corroboration of the structure proposed by Le Bel and Van't Hoff.

The problem of directed valence also arises in the H_2O molecule. The 8-electron configuration of the oxygen atom in the ground state is



The $2p_x$ -orbital is filled up and one unpaired electron is present in each of the p_y - and p_z -orbitals. The $1s$ -orbitals of two hydrogen atoms would overlap the p_y - and p_z -orbitals forming localised molecular σ -bonds. As p_y - and p_z -orbitals are at rt. angles, the two hydrogen atoms will form an angle of 90° between them [Fig. VI.8(a)]. But the experimental evidence indicates this angle to be 105° . The discrepancy is partly attributed to the polar nature of the molecule, for when the electron is drawn towards oxygen, the bare protons of the hydrogen repel one another and move away.

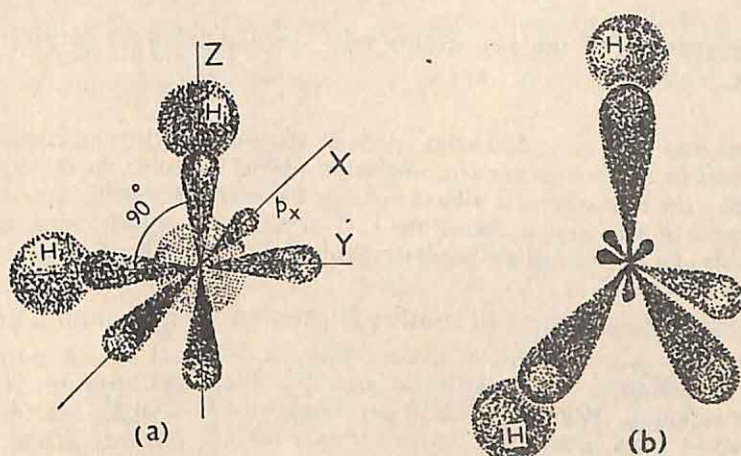


FIG. VI.8 (a) H_2O based on σ -bonding with separate p orbitals of oxygen
(b) H_2O based on sp^3 hybrid orbitals of oxygen

An alternative viewpoint is that the $2s$ - and $2p$ -orbitals of oxygen atom undergo hybridisation to yield four equivalent sp^3 -orbitals prior to bond formation. Two of these four sp^3 -orbitals are occupied by a pair of electrons each and do not contribute towards bonding, these are non-bonding orbitals. The remaining two sp^3 -hybrid orbitals accommodate one electron apiece and their electronic charge clouds overlap with $1s$ charge clouds of two hydrogen atoms forming H_2O molecule [Fig. VI.8(b)]. In such a case, the angle between H-atoms would be approx. 109.5° . It is now believed that the real state is an intermediate one, for 105° angle is feasible from a mix of $1:4$ proportion of s - and p -characters.

π -bonds. Besides sp^3 -hybridisation, orbitals of the carbon atom can undergo hybridisation in other ways. In ethylene type molecules and in aromatic molecules, the trigonal hybridisation or sp^2 -hybridisation is of utmost importance. A $2s$ -orbital of the carbon atom combines with $2p_x$ - and $2p_y$ -orbitals forming three identical trigonal hybrid orbitals inclined at 120° to each other in the same plane. This is sp^2 -hybridisation [Fig. VI.9(a)]. The unaffected p_z -orbital remains

perpendicular to the plane of the trigonal hybrids. In ethylene, two such C-atoms come together and one hybrid orbital from each atom overlaps to form a σ -bond, C—C. The other four hybrid orbitals of the two atoms are bonded with $1s$ -orbitals of separate H-atoms; these are also σ -bonds. The

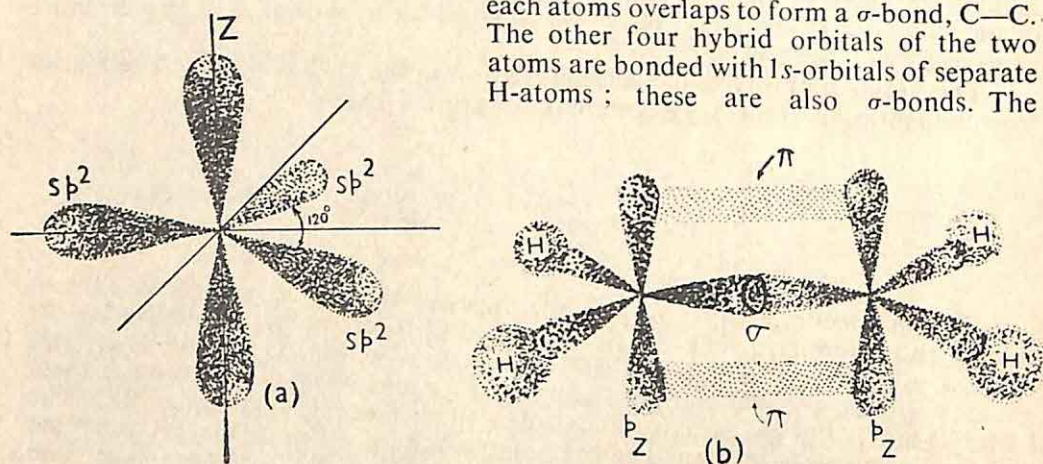


FIG. VI.9. Bonding in ethylene

remaining p_z -orbitals of the two atoms now overlap sideways to give rise to a π -bond [Fig. VI.9(b)].

A π -bond may then be looked upon as one in which the overlapping charge clouds are arranged parallel to the internuclear axis, whereas in σ -bond formation the cloud is symmetrically disposed. The formation of a π -bond not only increases the stability but also prevents the free rotation of CH_2 -groups round the C—C axes. So the double bond between the C-atoms consists of a σ -bond and a π -bond, the character of the two bonds being different.

Boron trichloride may be cited as another illustration for sp^2 -hybridisation.

Diagonal or sp -hybridisation occurs when a s -orbital and a p -orbital mix to give two equivalent hybrid orbitals at 180° . Such hybridisation is observed in acetylene linkages. When the s and p -orbitals of the C-atom are transformed into two hybrid ones, the other two p -orbitals remain unused. When two such carbon atoms link up, one of the hybrids from each takes part to form the σ -bond between them. The other two hybrids are bonded with $1s$ -orbitals of H-atoms. The p -orbitals then form a couple of π -bonds, as in Fig. VI.10. In fact, the two π -bonds from p_y and p_z -orbitals combine to form a sheath of electron density between the C-atoms.

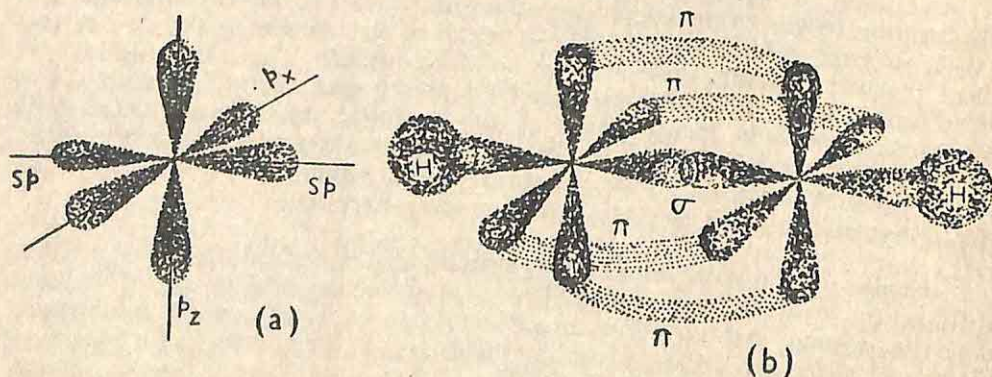
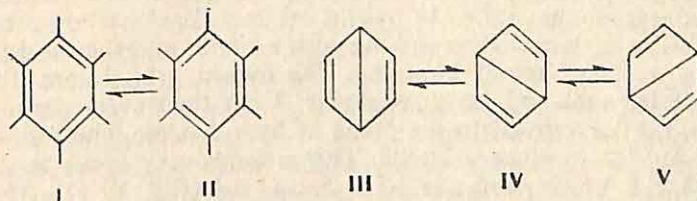


FIG. VI.10 Bonding in acetylene

VI.6. Resonance. Kekule's structure for benzene molecule may be represented as



Both the bond-diagrams I and II, having alternate double bonds are equally possible. Similarly possible are the three Dewar structures.

In all these configurations, the valency requirements of the constituent atoms are satisfied. What then is the structure of benzene molecule? The true structure of the molecule is a blend of all the possible forms. It should be realised that this does not mean that some molecules have one structure and some another. The molecule will have a structure intermediate between all the possible configurations. Such a conception of multiplicity of structures is called *resonance* and the true molecule is a *resonance hybrid* of the different forms. It may be noted that resonance is not a phenomenon, since the resonating forms do not have any real existence and there is no chance or idea whatsoever of the molecule assuming different canonical structure at different instants of time.

In different resonating forms of a molecule, only the electrons can have different arrangements but not the atoms. This is where it differs from isomerism. The number of unpaired electrons must also be the same in resonating structures.

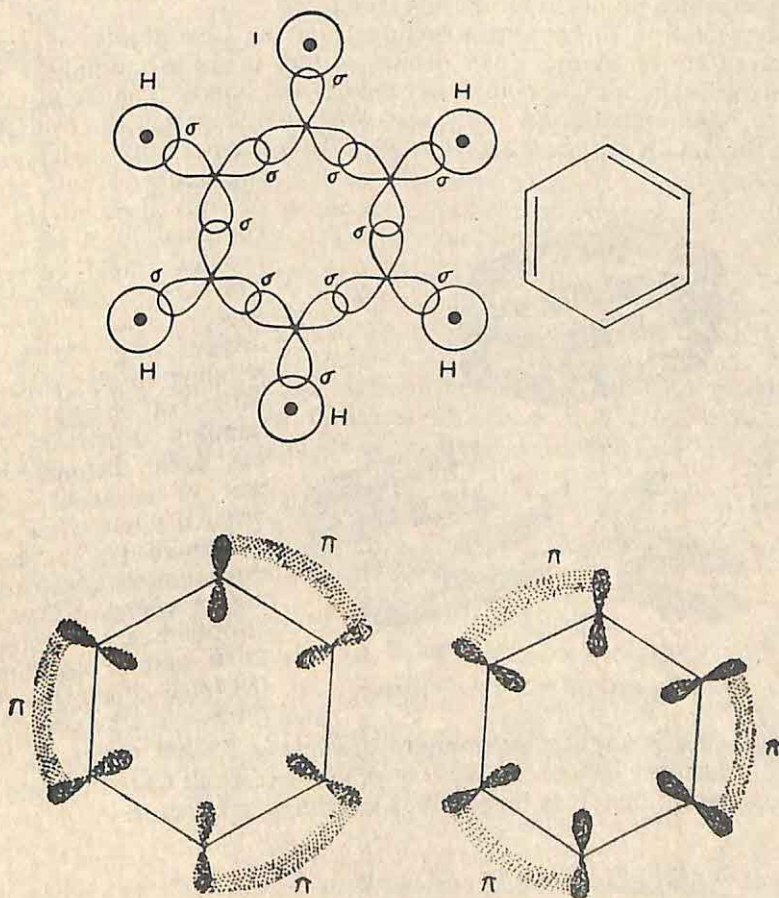
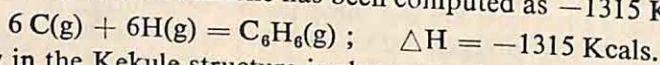


FIG. VI.11 The structure of benzene

A quantum-mechanical description of benzene structure may also be given. There is sp^2 -hybridisation in the atomic orbitals of all the six-carbon atoms. The six carbon atoms have thus 18 hybrid orbitals. Each carbon used two of the hybrid orbitals in carbon-carbon linking with σ -bonds and the third hybrid forms σ -bonding with 1s-orbital of H-atoms. The hybrid orbitals are thus all fixed and these are trigonal and hence coplanar. Even then every carbon atom has an unused p_z -orbital vertical to the plane of hybrid ones. These p_z -orbitals now overlap sideways to produce π -bonds. The π -bonds may occur between C-atom nos. 1-2, 3-4, 5-6, or between nos 2-3, 4-5, and 6-1 (Fig. VI.11). The two possibilities correspond to the two Kekule structures. In the same way Dewar structures may also be represented.

The heat of formation of benzene has been computed as -1315 Kcals.



The energy in the Kekule structure is also computed from the bond energies.

$$\begin{array}{rcl} 6 \text{ D}_{\text{C-H}} & = & 6 \times 98 \\ 3 \text{ D}_{\text{C-C}} & = & 3 \times 83 \\ 3 \text{ D}_{\text{C=C}} & = & 3 \times 146 \\ \hline & = & 1275 \text{ Kcals.} \end{array}$$

That is, benzene, contains a lesser energy of about 40 Kcals than that expected from the Kekule structure. This difference is known as the resonance energy and explains the stability of the molecule. Modern methods enable us to determine the bond-length. It has been found that the length of the bonds in benzene ($1.39 \text{ \AA}$) is intermediate between those of single and double bonds (C-C , $1.54 \text{ \AA}$; C=C , $1.34 \text{ \AA}$), a fact which points to resonating structures.

An interpretation of benzene structure from the view points of resonance has been given above. A molecular orbital picture of the π -bondings in benzene structure involves the idea of completely delocalised bonds. The six p_z , electrons of the six carbon-atoms occupy molecular orbitals in benzene, the orbitals being formed by the L.C.A.O. process (see p. 297). It will be readily understood that

the number of such molecular orbitals formed by linear combination of six p_z -atomic orbitals would be six (page 298) distributed over four energy levels. The three orbitals (Fig. VI.12), corresponding to the three lower values of energy are called bonding π -orbitals (π_1 , π_2 , π_3), each accommodating a pair of electrons. The six original p_z -electrons are thus accounted for. The other three π -molecular orbitals of higher energy values, called antibonding π -orbitals, remain vacant and are only occupied when the benzene molecules are excited.

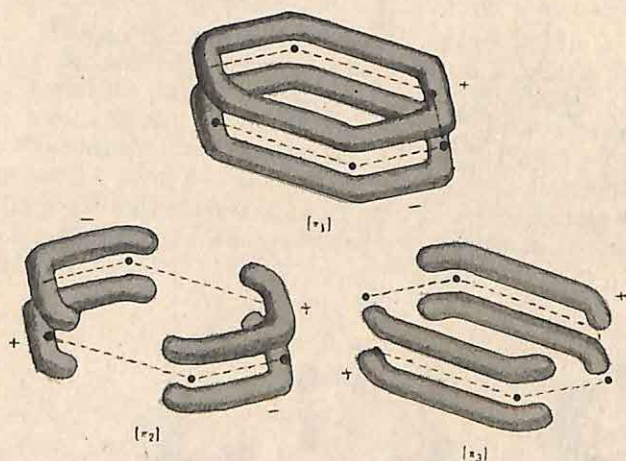
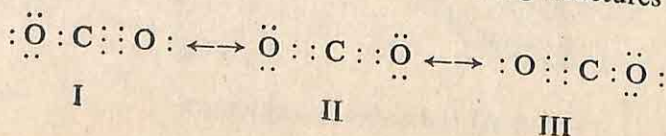


FIG. VI.12 Delocalised π -MO's of benzene

The resonance is not confined only to benzene or its derivatives; it is rather of frequent occurrence in various types of molecules. Even CO_2 molecule is supposed to be a hybrid one from three possible resonating structures;



VI.7. Heteronuclear Bonding. Electronegativity. In Sec VI.4, the covalent bond of the H_2 -molecule has been dealt. In the case of H_2 -molecule, the bond cemented two identical atoms or nuclei. The pair of electrons was equally influenced by the two nuclei, as such the distribution of electron density was symmetrical and alike around each nucleus. But when unlike atoms are bonded *i.e.*, in heteronuclear bonding, say in a gaseous hydrogen chloride molecule, the cementing pair of electrons is under influence of unequal fields and the charge cloud is not symmetrical. In all heteronuclear bonding, there is asymmetry in the distribution of electron density. Usually in common expression, we speak of electrons being shifted towards the more electronegative partner. The pictorial representation would be

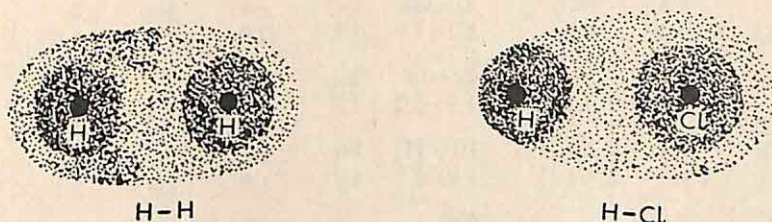


FIG. VI.13

The asymmetric distribution of charge cloud leads evidently to a polarity of the molecule, so that hydrogen chloride molecule is written as $H^{\delta+}-Cl^{\delta-}$. The covalent bond in hydrogen chloride is endowed with some amount of ionic character and is thus different from the covalent bond of H_2 -molecule or Cl_2 -molecule. All heteronuclear bondings have ionic property to some extent.

In view of this a rigid demarcation between a covalent bond and an ionic bond is not possible. In one extreme are the homonuclear bonds as in H_2 -molecule where ionic character is negligible, while at the other extreme in molecules like Na^+Cl^- , the covalent character being practically non-existent. The extent of the ionic character in a heteronuclear bond depends on the nature of the atoms bonded, *i.e.*, on their relative abilities of drawing the bond electrons towards their nuclei. This ability has been expressed as electronegativity of the atom.

Electronegativity. It is a measure of how powerfully a bonded atom attracts the electrons in the bond. Fluorine is the most electronegative and caesium is the least electronegative of elements. Pauling has enunciated a method for appreciation of electronegativities of elements. It has been suggested, the energy that the bond in $A-B$ would have, had it been purely covalent, is the geometric mean of the covalent bond energies of the atoms of the elements. Thus, the energy of the bond in $H-I$ is the geometric mean of the bond-energies of $H-H$ and of $I-I$;

$$D_{H-I} = \sqrt{D_{H-H} \cdot D_{I-I}}$$

But the observed bond energy is higher than the calculated hypothetical value, due to the ionic character of the bond. We find,

$$D_{H-I} = 71 \text{ Kcals (observed)}$$

and

$$D_{H-I} = 61 \text{ Kcals (calculated as above).}$$

Hence, the difference $\Delta = 10 \text{ Kcals} = 0.4 \text{ e.v.}$ energy is a measure of the ionic properties shown by the bond, due to difference in the electronegativities of the bonded atoms. Δ is thus a measure of the difference of the electronegativities of A and B, To be precise,

$$x_B - x_A = \sqrt{\Delta}$$

where x_A and x_B are the electronegativities of A and B respectively. This relation gives only a difference of electronegativities. In order to obtain the individual electronegativity, a standard value has been set for hydrogen, such that $x_H = 2.1$,

The electronegativity of iodine is then $x_I = 2.1 + 0.4 = 2.5$. Following this principle, Pauling ascertained the electronegativities of other elements as in the Table below.

THE ELECTRONEGATIVITY SCALE ($H = 2.1$)

Li 1.0	Be 1.5	B 2.0		C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5		Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti—Ga 1.7—1.9	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr—In 1.9—2.2	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La—Lu 1.1	Hf—Tl 1.9—2.3	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
	Ra 0.9		Th 1.3				

A direct method for calculating electronegativity x has been proposed by Mulliken, such that, $x = (I + A)/5.6$, where I and A are the ionisation potential and the electron affinity of the atom. Though arbitrary in nature, there is a concordance in the values obtained by Pauling's and by Mulliken's methods,

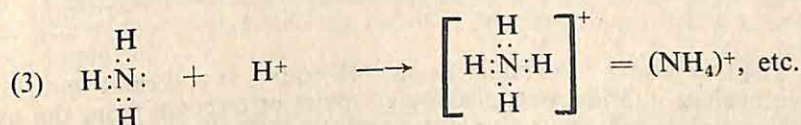
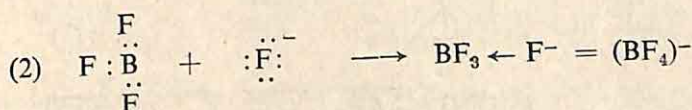
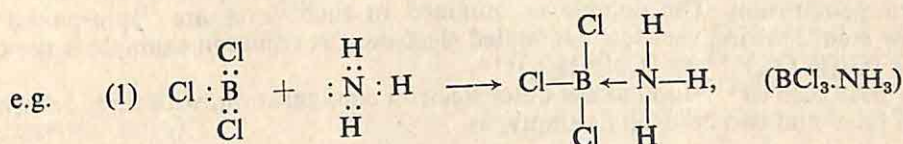
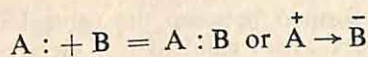
	H	F	Cl	Br	I
x (Pauling)	2.1	4.0	3.1	3.0	2.5
x (Mulliken)	2.5	3.8	3.0	2.8	2.4

The importance of these quantities lies in the fact that they at least qualitatively reflect the chemical behaviour of the elements. The greater the horizontal separation between two atoms in the electronegativity scale (see Table above) the greater is the ionic character of a bond between them. When the separation on the scale is 1.9, the bond is 50% ionic in character. Bonds containing hydrogen is generally quite strong as the hydrogen atom having no inner shell can come close to other atoms.

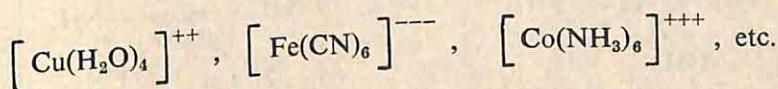
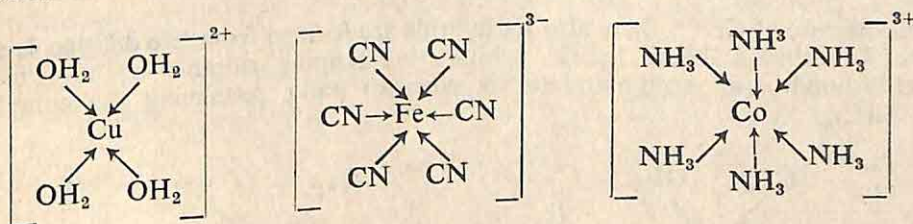
The bond between two highly electronegative atoms is covalent as in NO or CCl_4 . The bond linking two elements of low electronegativity is a metallic one as in Brass ($\text{Cu} + \text{Zn}$). The bond type between a highly electronegative and a low electronegative element is ionic as in KCl. Also, the greater the separation of two elements in the electronegativity scale, the stronger will be the bond between them. The heat-evolution in the formation of the bond is a measure of the bond-strength. Thus, we find,

	ΔH (Kcals)	$x_B - x_A = \sqrt{\Delta}$
$\text{H} + \text{F} = \text{HF}$	64	2.0
$\text{H} + \text{I} = \text{HI}$	1.5	0.4

VI.8. Dative Covalent Bond : Bonding in Complexes. We have seen that in a covalent bond between two atoms each atom contributes one electron to form the pair of electrons involved in the bond. But there are instances where one atom provides both the electrons required. Such a bonding is called a *dative covalent bond* and is necessarily polar to a large extent. In this type of bonding the *donor* atom must possess a pair of unused electrons. Such atoms are usually found in Groups V, VI and VII of the Periodic Table. The *acceptor* must possess at least one orbital empty. Highly charged metallic ions are also found to act often as good acceptors, such as Fe^{+++} , Co^{+++} etc. Electron rich molecules or ions such as NH_3 , H_2O , CN^- , Cl^- , NO , etc. act as good donors. The formation of a dative covalent bond may be represented as

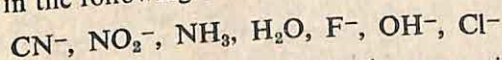


Instances of dative bonds are most frequent in the formation of complex ions. A complex ion is formed when a simple ion forms a covalent bond with another ion, molecule or atom. These electron rich ions or groups or molecules which give pair of electrons to the central metallic ion are called *ligands*. As common instances of dative covalency in complexes, we may cite



Bonding in Coordination Complexes : Stable complexes are obtained with ions of transitional elements, for, these ions are highly charged and thus produce strong electrostatic field for attracting ligands. For the stability of the complex it is also necessary to have strong bonding between the ligands and the central ion.

If the donor ligand is highly electronegative the resulting bond will be ionic and will dissociate in aqueous solution. Ligands which have low electronegativity will form dative covalency and the complex will not easily break in solution. The stability decreases in the following order



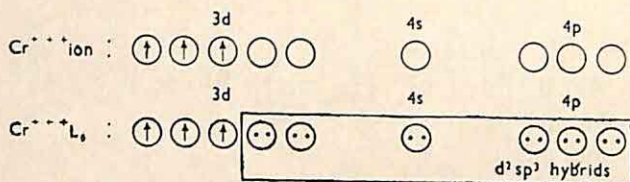
The charge carried by the complex is the algebraic summation of the +ve charge of the central metal ion and the -ve charges donated by the ligands. We have seen that the number of ligands attached to the central ion is mostly six, and in some cases it is four. Six-ligand complexes are all octahedral. Let us first examine how such complexes are formed.

In the formation of octahedral complexes, hybridisation involving *d* orbitals always occur. Pauling has proposed that it could be possible in two ways.

(a) d^2sp^3 -hybridisation : Two vacant *d*-orbitals of a shell along with one *s*-orbital and three *p*-orbitals of the next outer shell of the central ion combine to produce six hybrid orbitals. These six hybrid orbitals overlap with suitable ligand orbitals to form σ -bonds each of which accommodates a pair of electrons. Six

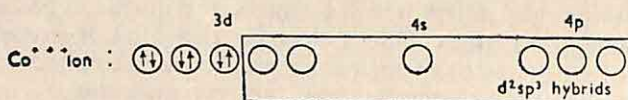
covalent bonds are thus formed between the central ion and the ligands. This type of hybridisation occurs with ligand of low electronegativity and have sufficient penetration. The complexes obtained in such cases are "spin-paired" or "low spin", having very few uncoupled electrons. A common example is the complex $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ or $[\text{Co}(\text{NH}_3)_6]^{+++}$.

The bare Cr^{+++} ion has the outer electron configuration, with three $3d$ -orbitals half filled and two $3d$ -orbitals empty, as

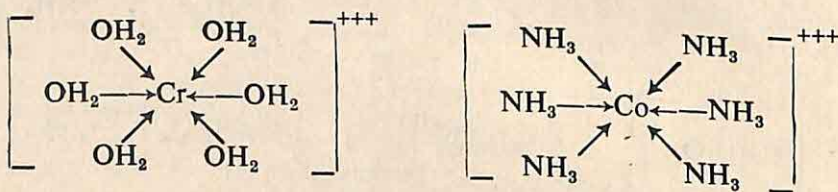


The two empty $3d$ -orbitals along with empty $4s$ and three $4p$ -orbitals produce six equivalent hybrids, occupied by six pairs of electron from the oxygen atoms of water molecules. The result is the complex, $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$.

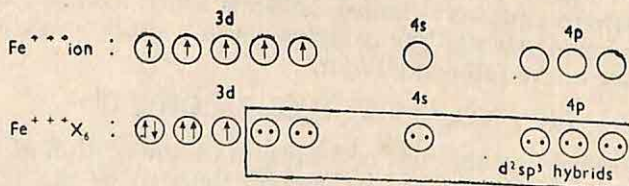
Similarly, Co^{+++} ion has the outer electron configuration as



As in the case of Cr^{+++} , here also six hybrids are formed from two $3d$, one $4s$ and three $4p$ orbitals. These hybrid orbitals overlapping suitable ligand orbitals form σ -bonds, and accommodate six electron pairs, producing the complex, $[\text{Co}(\text{NH}_3)_6]^{+++}$.



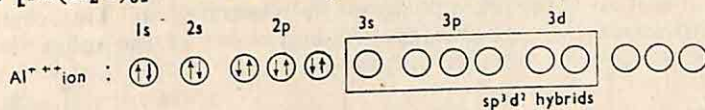
There are also cases where the ligands force out the unpaired electrons to make two of $3d$ -orbitals empty. The unpaired electrons thrown out couple with similar electrons in other $3d$ -orbitals, as we find in $\text{Fe}(\text{CN})_6$ complexes. The structure of ferric ion with five unpaired electrons in $3d$ -orbitals is



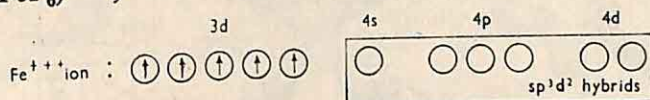
Two of the $3d$ -electrons are paired off and only one unpaired electron (low spin) is left and two $3d$ -orbitals become empty. Next the usual hybridisation fill them up carrying with them six negative charges. The electrons from CN^- ligands as a whole would carry now three negative charges. The result is, the complex $[\text{Fe}(\text{CN})_6]^{---}$.

(b) sp^3d^2 -hybridisation : This type of hybridisation is favoured by ligands having high electronegativity. The unpaired electrons are left undisturbed in such complex formation and these are called "spin free" or "high spin" complexes.

In these hybridisations, s , three p and two d -orbitals of the same shell are used, hence sp^3d^2 . $[\text{Al}(\text{H}_2\text{O})_6]^{+++}$ is an example of this type :

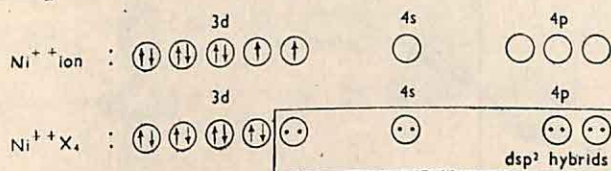


Similarly, in $(\text{FeF}_6)^{---}$,

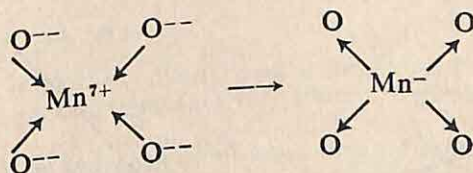
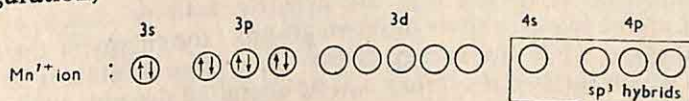


Experimental determination of the number of unpaired electrons in these compounds (which is the same as in the free ion) confirms the hybridisation proposed.

The four-ligand complexes geometrically have a planar or a tetrahedral configuration. The planar configurations result when dsp^2 -hybridisation occurs as with nickel complexes.



But when the $3d$ -orbitals are completely filled or completely empty, sp^3 -hybridisation occurs as in chromate or permanganate ions. This leads to tetrahedral configuration,



We thus see that the valency bond approach due to Pauling gives an adequate explanation for the formation of complexes. It has the strongest support from the study of magnetic properties of complexes. The number of unpaired electrons found from such studies confirm the theoretical predictions. But the weak point in Pauling's description is why with the same central ion sometimes d^2sp^3 and sometimes sp^3d^2 hybridisation become necessary. Besides the artificial prescriptions as to the nature of the bonds, the theory does not offer any explanation for the spectra of the complexes nor does it offer any possibility of explaining magnetic behaviour beyond specifying numbers of unpaired electrons. An alternative to the valency bond approach has later been proposed to explain complex-formation. This is the ligand-field theory.

Ligand field theory. According to this theory, the electrostatic interaction between the ligands and the d -orbital electrons of the central atom play the main role in the complex-formation and the electrostatic forces are to be taken into consideration. The ligands are electron-rich groups which project their electron pairs towards the positive central ion and electrostatic forces come into play. The d -orbital electrons of the central atom then tend to orient themselves in a fashion so as to avoid the ligand electrons as far as possible. According to theory, only the d -orbital electrons are to be considered, the question of hybridisation does not arise.

The d -orbitals take approximately the shape as shown in Fig. VI.14. When there are six ligands arranged octahedrally, two of the orbitals point towards the ligands, the other three takes positions in between them. The result is that the electrons of the two orbitals are repelled and those of the other three orbitals

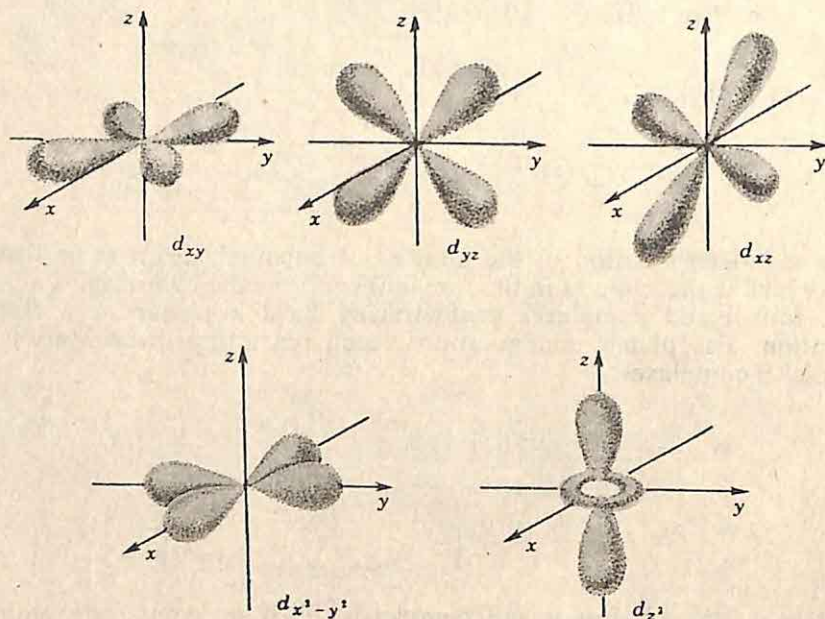


FIG. VI.14

remain uninfluenced. It means that the negative field produced by the ligand electrons split up the five d -orbitals into two groups : the energy of the two repelled orbitals is increased while the energy of the other three orbitals is little affected. The extent to which the two d -orbitals will be energised depends upon the ligands,

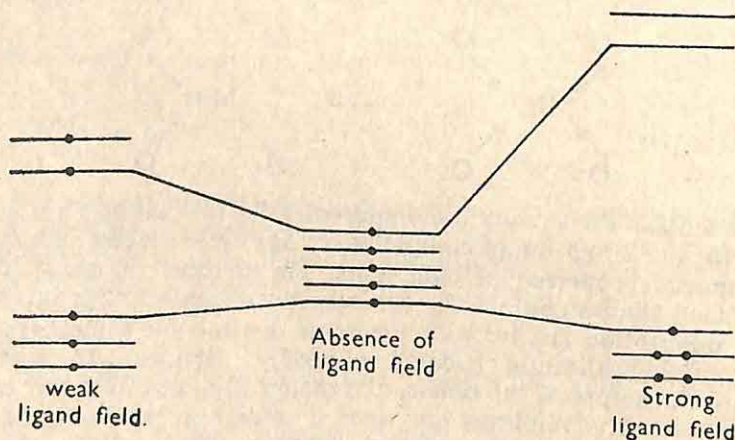


FIG. VI.15

or more precisely, upon the electronegativity of the ligand. With a high electro-negative donor ligand, the ligand-field is weak, the "splitting" is relatively less and the unpaired electrons in d -orbitals remain undisturbed. On the other hand, with a strong ligand field, the splitting is much greater. In a high electrostatic field, the unpaired electrons, in order to make themselves stable, pair off with similar ones. Diagrammatically this may be represented as in Fig. VI.15.

Let us take the ferric ion (Fe^{+++}). With six water molecules as ligands as in $[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$, the field is weak, and in consequence, the five d -orbital electrons remain distributed in all the five orbitals. But when the ligand is $(\text{CN})^-$ as in

[Fe(CN)]⁻⁻⁻ the strong field causes a large splitting ; the electrons of two orbitals are repelled to move away to other orbitals to form stable pairs. This is how ligand field theory explains the two types of ligand bonding in complexes. These are consistent with experimental observations in respect of spectroscopic and magnetic studies. The two theories are based on entirely different reasonings but the ultimate conclusions are the same.

Chelate groups. There are instances where the ligands have more than one group projected to the central metal ion. This gives a particular stability to the molecules and internal ring structures are automatically developed. A common example is that ethylene diamine forming complex with Cu⁺⁺ ions, as

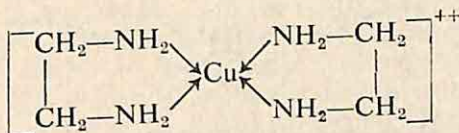


FIG. VI.16

Such groups are called chelates and the resulting products as chelate complexes. In alkaline medium, dimethyl glyoxime chelates with Ni⁺⁺ ions forming a precipitate, Fig. VI.17 which is particularly stabilised through hydrogen bonds (see next section).

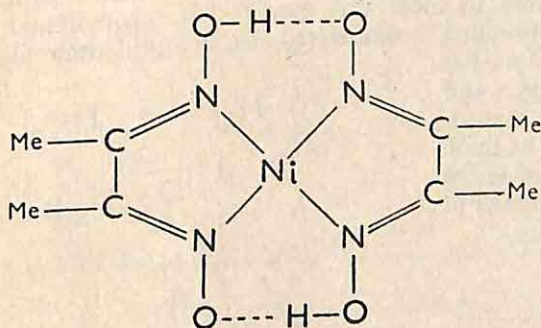


FIG. VI.17

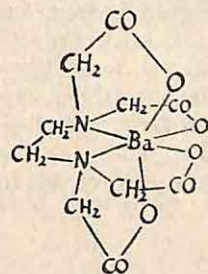
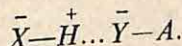


FIG. VI.18

Similarly EDTA [Ethylene diamine tetra acetic acid] forms chelates with various metal ions, rendering them into very stable complexes Fig. VI.18.

VI.9. Hydrogen Bond. A hydrogen atom when bonded with a highly electronegative atom such as fluorine, oxygen etc. acquires a positive charge. In consequence of this, such a hydrogen atom exerts an electrostatic attraction on other highly electronegative atom like fluorine, nitrogen or oxygen. There is thus a dipole-dipole or dipole-ion attraction, which has been given the name, *hydrogen bond*. This may be represented as,



where X and Y are strongly electronegative atoms of fluorine, oxygen or nitrogen. The broken line indicates the electrostatic interaction or hydrogen bond. The full lines are covalent bonds.

The hydrogen bond, a sort of polar link, is formed as the attraction between H and Y outweighs the repulsion between X and Y . But Y must be a small electronegative atom such as of fluorine, oxygen or nitrogen. Hydrogen bonding with chlorine, sulphur or carbon is rarely observed because of the large size of the atoms.

Such a bonding is significant only with hydrogen because of the minute size of the almost bare proton which enables Y to make a close approach to the positive charge. The bond cannot be regarded as a covalent one for (i) a hydrogen atom can accommodate only two electrons in its $1s$ orbital ; use of $2s$ orbital would involve much higher energy. (ii) The experimentally measured bond energy for

hydrogen bond is much less than that of a covalent bond. It approximates to 6 Kcals only, about 10% of that of a covalent link.

(iii) The bond length of hydrogen bond computed from spectroscopic and diffraction measurements is found to be greater than that of a covalent bond except in $[\text{HF}_2]^-$. In a bond like —O—H...O— the hydrogen atom is not located at the middle of the two oxygen atoms.

The outstanding effect of hydrogen bonding is observed in molecular association. Thus hydrogen fluoride even in gaseous state is highly associated as $(\text{HF})_n$, due to hydrogen bonding, as

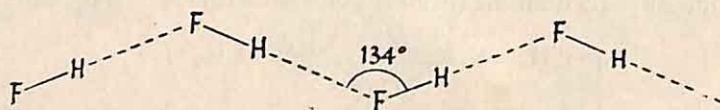
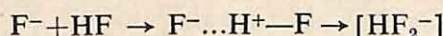


FIG. VI.19 Hydrogen bonding in HF (Dotted lines are hydrogen bonds.)

In aqueous solution too, fluoride ion forms $(\text{HF}_2)^-$ ion through a hydrogen bond,



Liquid water shows many abnormal physical properties ; such as, high boiling pt. considering its mol. wt., high latent heat of vaporisation, surface tension, etc. These abnormalities are attributed to molecular association through hydrogen bonding. The effect of hydrogen bonding is manifested also in liquid ammonia and some liquid hydroxy compounds. Ice has a peculiar structure in which every water molecule is hydrogen-bonded tetrahedrally to four others, as in Fig. VI.20. Such an open structure shut in a lot of space and when ice melts, there is shrinkage in volume with increase in density :

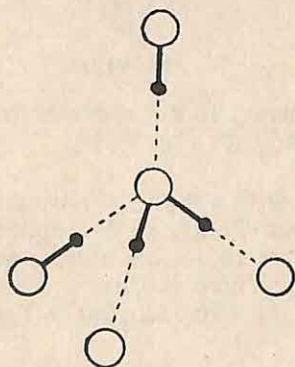


FIG. VI.20 Structure of ice

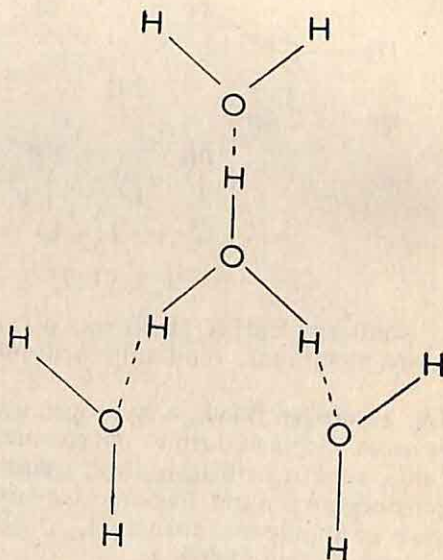
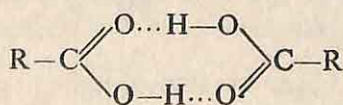
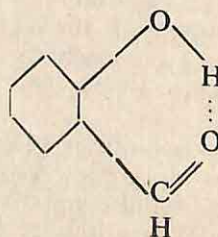


FIG. VI.20a OH holding three water molecules by hydrogen bonds

Intermolecular association through hydrogen bonding is often found in organic alcohols or carboxy acids.



(Dimerisation)



Salicylaldehyde

Even intramolecular hydrogen bonding is possible with some molecules as in nitrophenol or salicylaldehyde

There is, besides those mentioned above, another type of bonding, commonly named "*metallic bond*." A description of this type of bonding has already been narrated in Sec. III.13(d).

VI.10. Bond-energies and Bond-lengths. We have already seen how bond energies can be obtained from thermochemical measurements [Chapter IV. Sec. 20]. The bond energies of simple diatomic molecules can also be computed from the potential energy curves or from force constants spectroscopically measured.

As to bond lengths, we have found in Sec III.14, how the atomic and ionic radii in crystals are obtained from X-ray diffraction in crystals. Electron diffraction, and now neutron diffraction too, enable us to find out the bond-lengths. Studies of the molecular spectra of simple molecules also provide us with moment of inertia from which bond distances can be calculated. These will be discussed in subsequent chapters. The bond-lengths of some common diatomic molecules and of a few interesting bonds are tabulated below.

BOND LENGTH (in Å)			
Molecule	Bond-length	Bond	Bond-length
F ₂	1.42	C—C (ethane)	1.54
Cl ₂	1.99	C—C (graphite)	1.42
Br ₂	2.28	C—C (benzene)	1.39
I ₂	2.67	C—C (ethylene)	1.34
O ₂	1.21	C—C (acetylene)	1.20
H ₂	0.74	O—H	0.96
HCl	1.27	C—S	1.82
HBr	1.41	I—Cl	2.32
HI	1.61	N—O	1.15

Suggestion for further reading

- (i) *Electronic theory of valency* : SPEAKMAN (Arnold 1955)
- (ii) *The nature of chemical bond* : Pauling (3rd Edn., Oxford)
- (iii) *Valence* : COULSON (Oxford, 2nd Edn.)
- (iv) *Modern aspects of inorganic chemistry*, Chap 3 : EMELIUS & ANDERSON
- (v) *Introduction to ligand field theory* : BALLHAUSEN

Problems

1. Suggest structural formula for NH₃, NO₃⁻, SF₆, NO, CO.
2. Indicate possible resonance structures for HNO₃, H₃PO₄, CH₃COO⁻, N₂O and benzene.
3. Explain σ - and π -bonding. Indicate such bondings in N₂, C₂H₄ and C₆H₆.
4. What is a hybrid bond? Show how hybrid bonds explain the structures of PF₅, CO(NH₃)₆⁺⁺, CH₃Cl.
5. Explain what is meant by a hydrogen bond? Show how such a bond considerably influences the properties of water.

PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

In studying the structure of a molecule, the problem is to find out the size and shape of the molecule and the geometry of the arrangement of its constituent atoms. For this purpose we need to determine the lengths of the bonds or interatomic distances and the bond angles. We also need to ascertain the type of atomic and other motions as well as the distribution of electrons around the nuclei. A theoretical approach for such information even for a diatomic molecule would be too complicated. On the other hand, the chemical analysis and determination of mol. wt. would reveal the composition of the molecule, while a study of its chemical properties would enable us to ascertain the groups or sequence of atoms in the molecule. These will not help us in finding out the structure of the molecule. To obtain information as to the configuration of the molecule, it is necessary to fall back upon a study of its typical physical properties such as refractivity, absorption or emission of radiations, electrical polarisation, etc. We have seen in connection with crystals how the interatomic distances and arrangement of atoms in the lattices are obtained from an application of X-rays and electron diffraction studies. In this chapter we intend to discuss briefly the refined methods now-a-days employed to find out the molecular structure. Very often several methods are to be used jointly to have an idea of the structure ; any one method would lift the veil only a little.

A. PARACHOR

VII.1. Parachor. Macleod's equation (II.19), which is an empirical relation between the surface tension (γ) and density (D) of a liquid, has been found to be valid for a considerable range of temperature,

$$\frac{\gamma^{\frac{1}{4}}}{(D-d)} = c \text{ (constant)} \quad \dots \text{ (II.19)}$$

where d is the density of its vapour at the same temperature.

Multiplying both sides by M , the mol. wt. of the substance,

$$\frac{M\gamma^{\frac{1}{4}}}{(D-d)} = M.c = P \text{ (constant)} \quad \dots \text{ (VII.1)}$$

since both M and c are constants for a given substance.

It is remarkable that the constant P , called its "*parachor*", is quite independent of temperature (Sugden, 1924). If the vapour density d , which is often quite small, be neglected, then

$$P = \frac{M}{D} \gamma^{\frac{1}{4}} = V \cdot \gamma^{\frac{1}{4}} \quad \dots \text{ (VII.2)}$$

where V = molar volume of the substance.

It is obvious that at temperatures where the surface tensions of two liquids are the same, their parachors would be proportional to their molar volumes. Further at a temperature where the surface tension of a liquid tends to unity, parachor becomes the molar volume. A knowledge of this property thus gives us an idea of molar volume, V . The cross-section of the molecule will evidently be proportional to $P^{\frac{3}{4}}$.

It was soon found that (i) parachors of many isomeric substances were identical and that (ii) the difference in parachor values of successive members in a homologous series was found to be constant, irrespective of the nature of the series.

TABLE : PARACHORS

Isomers	P	Homologous series					
		Hydrocarbons			Esters		
			P	ΔP		P	ΔP
Amyl formate	293.6	C ₂ H ₆	110.5		C ₂ H ₄ O ₂	138.1	
Ethyl butyrate	293.6	C ₃ H ₈	150.8	40.3	C ₃ H ₆ O ₂	177.3	39.2
Butyl acetate	295.0	C ₄ H ₁₀	190.0	39.2	C ₄ H ₈ O ₂	216.1	38.8
Propyl propionate	295.0	C ₆ H ₁₄	270.1	40.0 × 2	C ₆ H ₁₂ O ₂	293.8	38.8 × 2
Ortho xylene	283.3	C ₇ H ₁₆	309.3	39.2	C ₇ H ₁₄ O ₂	332.3	38.5
Meta xylene	283.3						
Para xylene	283.3						

It leads to the inescapable conclusion that parachors are additive functions of the chemical composition. The contribution of a CH₂-group to the parachor value is about 39. The molar parachor would be the sum of the atomic parachors. On this assumption, the parachor value of hydrogen, P_H , would be,

$$P_{C_nH_{2n+2}} = nP_{CH_2} + 2P_H = 39n + 2P_H$$

Substituting the experimental value of the parachor of the paraffin C_nH_{2n+2} , the atomic parachor *i.e.*, parachor equivalent of a hydrogen atom was found to be 17.1. So, the atomic parachor of a carbon atom is

$$P_C = P_{CH_2} - 2P_H = 39 - 2 \times 17.1 = 4.8$$

In this way, the parachor-equivalents of different atoms have been calculated as given in the table below.

A comparison of the parachor values calculated from atomic parachor-equivalents with those experimentally observed showed a divergence in the cases of unsaturated and ring compounds. It meant that the parachors are not only additive but also constitutive. The parachor of ethylene C₂H₄ was experimentally found to be 99.5, while the calculated value of 2CH₂-groups was 78, the difference being 21.5. From a study of different olefinic compounds, the contribution of a double bond towards parachor has been taken as 23.2. The parachor value of a single bond has been taken as zero and those for other bonds and rings are as given in the table.

TABLE : ATOMIC AND STRUCTURAL PARACHOR EQUIVALENTS

Element	P	Element	P	Structure	P
C	4.8	S	48.2	Double bond	23.2
H	17.1	Cl	54.3	Triple bond	46.6
N	12.5	Br	68.0	6-membered ring	6.1
O	20.0	I	90.0	5-membered ring	8.5
P	39.2	O ₂ in ester	60.0	4-membered ring	11.6
				Naphthalene ring	12.2

We can now illustrate the usefulness of parachor studies in the elucidation of molecular structure.

Structure of Benzene : The observed parachor of benzene is 206.2. If Kekule formula be accepted, its parachor value may be calculated as

$$\begin{aligned}
 6 \text{ C-atoms} &= 6 \times 4.8 \\
 6 \text{ H-atoms} &= 6 \times 17.1 \\
 1 \text{ six-membered ring} &= 6.1 \\
 3 \text{ double bonds} &= 3 \times 23.2
 \end{aligned}$$

$$\text{Total } P = 207.1$$

The Kekule structure is thus supported.

the half of the field which was formerly bright would be completely dark now and the other formerly dark half would now be bright. In an intermediate position, the entire field of view will have uniform brightness (or darkness). The polarimeter is set at this position, *i.e.*, this is the zero-position of the polarimeter and the reading is taken from the circular disc provided with an angular scales.

The liquid or the solution whose optical activity is to be measured is then taken in a tube of fixed length (usually 10 cms or 20 cms) and placed in between the polariser and the analyser and co-axially with them. The liquid turns the plane of polarised beams and as such the field of view will be illuminated now non-uniformly, as seen through the telescope. The analyser is now rotated till the field becomes one of uniform illumination as before. The new position is read from the scale. The difference of the two readings is the angle through which the polarised beam has been rotated by the liquid or the solution. Thus we can ascertain the optical activity of the substance; the angle of rotation certainly depends on its nature. For a complete detail of the method, a practical text-book should be consulted.

The magnitude of rotation depends upon several factors: (i) the density or concentration of the substance, (ii) the temperature, (iii) the wavelength of the light and (iv) the length of the substance through which the beam has to pass.

The rotatory power of the substance is expressed in terms of specific rotation, $[\alpha]_{\lambda}^t$ such that

$$[\alpha]_{\lambda}^t = \frac{\alpha}{l \cdot d}$$

where α is the observed rotation of polarised beam at $t^{\circ}\text{C}$ caused by l -decimeters of liquid (density, d). λ is the wavelength of light used.

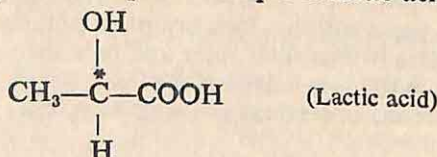
In the case of a solution of conc. c expressed in gms per cc.

$$[\alpha]_{\lambda}^t = \frac{\alpha}{l \cdot c}$$

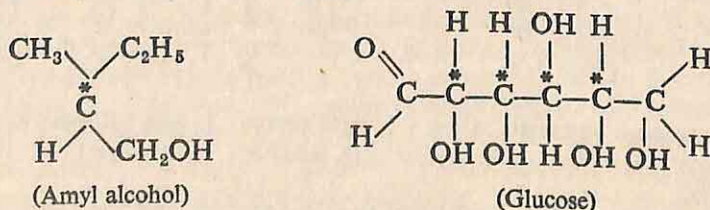
The specific rotation is thus the rotation produced by a solution containing 1 gm of the substance per c.c. when the length of the column through which the light passes is 10 cms. The specific rotation is a characteristic property of the optically active species. The molar rotation has been defined as

$$[\alpha_M]_{\lambda}^t = \frac{M}{100} \cdot [\alpha]_{\lambda}^t \quad \dots \text{(VII.3)}$$

Van't Hoff and Le Bel independently pointed out the connection between the optical activity and the asymmetry present in the molecule of the substance (1874). Most of the optically active substances are organic compounds whose molecules contain at least one carbon atom having its four valences satisfied with four different radicals or atoms. Such a carbon atom is called an asymmetric C-atom (marked with asterisk below). The simplest example is lactic acid,



Other examples may be cited, *e.g.*,



[Such molecular asymmetry is also known in some inorganic compounds containing nitrogen, sulphur, etc. A few organic compounds having no asymmetric C-atom have also been found

optically active due to asymmetric formation of the molecule itself in space, such as, in a spiral type of molecule.]

According to Van't Hoff, the four valences of C-atom are directed towards the corners of a tetrahedron, carbon remaining at the centre. If all the four groups are different, it is possible to show with space models that there are two ways of arranging these groups so that one is the mirror image of the other and these cannot be superimposed. When one of these turns the light towards the right, the other turns it to the left. Evidently the chemical and physical properties of the two forms are almost the same except that one is *dextro-rotatory* and the other *laevo-rotatory*. If an equimolecular mixture of the two forms is taken, the rotation of the two would counteract one another and no optical activity would be observed. Such a mixture is *racemic form* (*dl*) or the externally compensated form. Optically active compound synthesised in the laboratory are obtained in the racemic form. Organic chemists have however developed some methods for the resolution of the racemic mixture into dextro- and laevo-forms. If two asymmetric C-atoms be present in the molecule such that one atom causes a dextro-rotation and the other laevo, the optical activity will be reduced. Moreover, if the radicals or atoms attached to the two C-atoms be identical as in tartaric acid, the optical activity will be nil due to internal compensation of rotation. Such internally compensated form is called the *meso-form*. Thus, for tartaric acid we have four varieties :

- | | |
|----------------|--|
| (i) dextro-, | both C-atoms turn the light to the right. |
| (ii) laevo-, | both C-atoms turn the light to the left. |
| (iii) meso-, | one C-atom turns the light to the right and other to the left. |
| (iv) racemic-, | an equimolecular mixture of <i>d</i> - and <i>l</i> -forms. |

Each optically active site presents two possibilities—a left and a right handed form. Thus, glucose containing four asymmetric C-atoms will have 2^4 or 16 forms. The study of optical activity thus gives us an idea of the spatial configuration of some molecules. In fact such studies had been most helpful in confirming the structure of different sugar molecules.

C. MAGNETIC ROTATION

VII.3. All transparent substances when placed in a magnetic field are capable of rotating a plane polarised beam passing through it along the lines of force. This is a general property of all transparent substances first observed by Faraday, hence often called Faraday effect. The direction of rotation of the polarised beam is dependent on the direction of lines of force.

Experimental measurements, made chiefly by Verdet and others, have shown that the extent of rotation caused by a given liquid is directly proportional both to the field-strength (H) and the length (l) of the column of liquid through which the polarised beam passes. Hence, the angle of rotation α is given by

$$\alpha = \omega l H \quad \dots (VII.4)$$

where ω , called *Verdet constant*, depends on the nature of the substance. Since $\omega = \alpha$, when $l = 1$ and $H = 1$, the Verdet constant is the rotation caused by one centimetre column of a liquid in a field of 1 gauss. The constant, though independent of temperature, varies with wave-length of the beam. Water is used as the standard material for comparing magnetic rotation due to different substances and the Verdet constant for water is $0.01312'$ min. of arc for sodium D-line.

The relative molar magnetic rotation (R_M) has been defined by the expression,

$$\left[R_M \right] = \frac{M \times \alpha \times \rho_0}{M_0 \times \alpha_0 \times \rho} \quad \dots (VII.5)$$

where M , α and ρ are the mol. wt., rotation and density for the given substance and M_0 , α_0 and ρ_0 are the same quantities for water, the same apparatus and conditions being employed. Since $M_0 = 18$ and $\rho_0 = 1$,

$$\left[R_M \right] = \frac{M \times \alpha}{18 \times \rho}$$

The absolute molecular magnetic rotation (r_m) is obtained by multiplying the above with the value for water

$$\text{i.e., } r_m = \frac{M \times \alpha}{18 \times \rho} \times 0.01312 \text{ min.}$$

It was W. H. Perkin who first pointed out the connection between magnetic rotation and structure of organic molecules. Perkin used a strong electromagnet in the pole-pieces of which were holes carrying the polarimeter tube. Now-a-days usually coils are wound round the polarimeter tube and powerful current is passed to produce the necessary field. A study of the rotations of the members of different homologous series revealed that addition of every CH_2 -group causes an average increase of 1.023. The magnetic rotation can then be expressed as

$$[R_M] = 1.023 n + S$$

where n is the number of CH_2 -groups and S is a series constant which varies with the homologous series. The series constants for different homologous families are

Homologous Series	Series constant, S
Paraffins	0.508
Primary alcohols	0.699
Ketones	0.375
Fatty acids	0.393
Esters	0.337 etc.

The knowledge that a CH_2 -group contributes 1.023 towards molar magnetic rotation, enables us to evaluate the contribution for different atoms. Thus r_m for hydrogen is 0.254 ; for carbon 0.515 ; for chlorine, 1.734 etc. The property of magnetic rotation is not purely additive but also to some extent constitutive. This is evident from the fact that geometrical isomers have different molar magnetic rotations, the fumaroid structures have higher values and that unsaturation leads to higher values for magnetic rotation, e.g., acetaldehyde $R_M = 2.40$, ethylene oxide, $R_M = 1.94$.

The study of magnetorotatory equivalents has been useful in the structural problems of terpenes and in some keto-enol tautomerism.

D. MOLAR REFRACTION

VII.4. In 1880, starting from Maxwell's electromagnetic theory of light, Lorenz and Lorentz independently deduced a relation between density (d) and refractive index (n) of a substance expressed in the form,

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} = R_s \quad \dots \text{ (VII.6)}$$

R_s is called the specific refraction of the substance and is independent of temperature. Moreover the specific refraction has also been found to be almost the same both for the liquid and gaseous state of the substance. The value of R_s however changes with the wavelength of the light used to measure the index of refraction, n .

Multiplying both sides of this relation by the mol. wt. M of the substance, we obtain the molar refraction, R_M ;

$$R_M = M \times R_s = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \quad \dots \text{ (VII.7)}$$

Since the refractive index n , being a ratio of velocities, is a dimensionless quantity, the molar refraction R_M has units of volume and is usually expressed in c.cm per mole. The refractive index is often accurately determined with the help of a Pulfrich or immersion refractometer.

The molar refraction is partly additive and partly constitutive. When the molar refractions of successive members of a homologous series are measured, the increase in the value of R_M for each addition of CH_2 group is found to be the same, i.e., the property is an additive one. The contribution of a CH_2 group is 4.618 with Na-D line. Subtracting the contribution of 6CH_2 groups (6×4.618) from the observed molar refraction of hexane, C_6H_{14} , we obtain the contribution made by two H-atoms. The refraction equivalent of a H-atom was thus found to be 1.100. The atomic refraction equivalent of carbon is $4.618 - 2 \times 1.100 = 2.418$. The refraction equivalents of some atoms and structures are listed here.

REFRACTION EQUIVALENTS (R_D)

H	1.100	O (carbonyl)	2.211	Double-bond. (C=C)	1.733
C	2.418	O (ether)	1.644	Triple bond (C≡C)	2.398
Cl	5.967	O (hydroxyl)	1.522		
Br	8.865	N (Primary amines)	2.322		
I	13.900	N (Secondary amines)	2.499		
S (sulphides)	7.97	N (Tertiary amines)	2.840		

That additivity is permissible in computing molar refraction is confirmed from the agreement between observed and calculated results. Thus,

	acetic acid	acetone	chloroform	diallyl	benzene	allyl alcohol
Calc.	12.91	16.07	21.42	28.78	26.31	17.11
Obs.	12.93	16.15	21.40	28.77	26.15	16.97

The presence of a double or a triple bond raises the molar refractivity showing its constitutive character. The benzene ring however has very little influence on the molar refraction.

There are instances where the observed molar refraction is much higher than the calculated one. Such exceptions occur in molecules with conjugated double bonds partly or wholly in open chains. To illustrate: The calculated and experimental molar refractions of diallyl agree quite well; but in the case of its isomer, isodiallyl, the calculated value is much less than that observed:

		$M_{R(a)}$	
		obs. :	calc.
Diallyl,	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$,	28.77	28.78
Isodiallyl	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$,	29.87	28.78 ($\Delta=1.09$)

Such discrepancies are also found in other systems with conjugated double bonds such as styrene, acetophenone etc. The conjugated double-bonds in the closed benzene ring has no effect, but those in naphthalene, anthracene etc. have marked effect. Such anomalous increase in molar refraction due to presence of conjugated double bond is called *optical exaltation*.

Mixtures. If two substances of mol. wts. M_1 and M_2 are mixed, the molar refraction of the mixture $[R_M]_{1,2}$ is presented by

$$[R_M]_{1,2} = \frac{n_m^2 - 1}{n_m^2 + 2} \cdot \frac{M_1 x_1 + M_2 x_2}{d_{mix}} \quad \dots \text{(VII.8)}$$

where x_1 and x_2 are the mol-fractions of the components present and n_m and d_{mix} are the refractive index and density of the mixture. It has however been found that $[R_M]_{1,2}$ is the sum of the individual molar refractions i.e.,

$$[R_M]_{1,2} = x_1 [R_M]_1 + x_2 [R_M]_2$$

$$= x_1 \cdot \frac{n_1^2 - 1}{n_1^2 + 2} \cdot \frac{M_1}{d_1} + x_2 \cdot \frac{n_2^2 - 1}{n_2^2 + 2} \cdot \frac{M_2}{d_2} \quad \dots \text{(VII.9)}$$

This relation is most often employed in obtaining refractive indices of solid substances, by dissolving them in solvents of known n and measuring the refractive index of the mixture. Application of molar refraction has been of considerable benefit in structural problems of some terpenes and camphors ; especially the exaltation indicated the presence of conjugated double bonds in them.

E. MOLAR POLARISATION : DIPOLE MOMENTS

VII.5. Polar and Non-polar Molecules. Molecules are composed of positively charged nuclei and negatively charged electrons distributed in space. The structural arrangement of these particles is different for different molecules. It will be easily conceived that the centre of gravity of the positive nuclei may or may not coincide with that of the negative electrons. When the centre of gravity of the positive charges in a molecule is exactly at the same point as that of the electrons, it is a *non-polar molecule*. Instances of non-polar molecule are found in H_2 , Cl_2 , N_2 , CO_2 , CH_4 , C_6H_6 , etc. On the other hand in many molecules, like those of HCl , CH_3Cl , $CHCl_3$, $C_6H_5NO_2$, H_2O , NH_3 , etc. the centres of gravity of the positive and the negative charges do not coincide ; such molecules are said to be *polar molecules*.

Since the molecule as a whole is neutral, if we have a total charge $+e$ at the centre of positive charges, the charge at the centre of negative charges would be $-e$. If l be the distance between the two centres of gravity in a polar molecule, it is said to have a permanent electric moment called the *dipole moment* (μ), given by

$$\mu = e \times l \quad \dots (VII.10)$$

In a non-polar molecule the distance $l = 0$ so that the dipole moment is nil.

VII.6. Electrical Polarisation. We shall first consider the non-polar molecules. When a non-polar molecule is placed in an electric field between two charged plates the latter will attract the positive nuclei towards the negative plate and the electrons towards the positive plate. In consequence the positive and negative centres would no longer be coincident [see Fig. VII.3(a)]. There will be an electrical distortion of the molecule to form an electrical dipole. Such distortion is called *distortion polarisation or electrical polarisation*. The distortion however disappears as soon as the field is withdrawn. It is thus an *induced polarisation* and the moment that the induced dipole would acquire during the application of the field is the induced moment, μ_i . The induced moment is directly proportional to the field strength X and is given by $\mu_i = \alpha X$,

$$\dots (VII.11)$$

where the constant of proportionality (α) is called the *polarisability* of the molecule. That is, α is a measure of the moment induced by unit field.

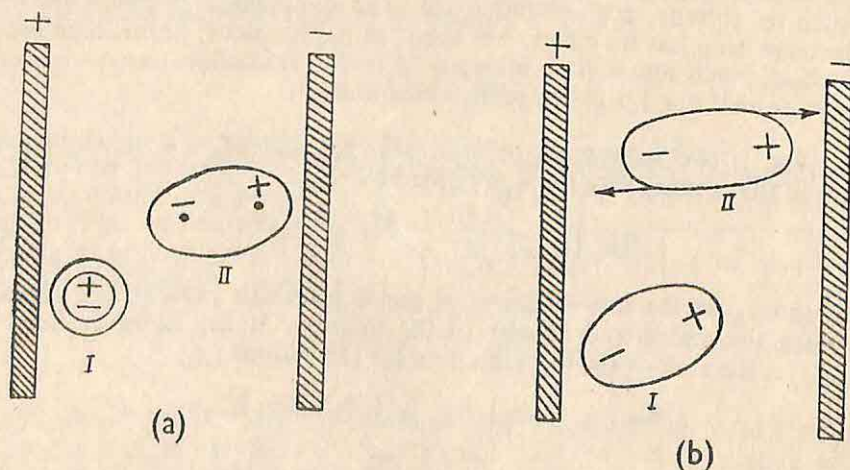


FIG. VII.3

Clausius and Mosotti established, from the electromagnetic theory, a relation between polarisability (α) and the dielectric constant (D) of a medium between the charged plates, in the form

$$\frac{4}{3} \pi N_0 \alpha = \frac{D-1}{D+2} \cdot \frac{M}{\rho} \quad \dots \text{(VII.12)}$$

N_0 , Avogadro number, M , molecular weight and ρ , density of the substance [see appendix 4]. The right hand side of this relation is called the *molar polarisation*. In a non-polar molecule, the polarisation is all induced. Hence the *induced molar polarisation* (P_i) may be written as

$$P_i = \frac{4}{3} \pi N_0 \alpha = \frac{D-1}{D+2} \cdot \frac{M}{\rho} \quad \dots \text{(VII.13)}$$

P_i is the electrical distortion caused in 1 mole of the substance by a unit field.

Since N_0 and α are independent of temperature, P_i will also be independent of temperature. Again D is a dimensionless number and hence the polarisation will be expressed in units of volume.

The dielectric constant (D) can be determined by finding out the capacitance of a parallel plate condenser with and without the substance as medium, for, $D = C/C_0$, where C is the capacitance with the substance and C_0 in vacuo. The mol. wt. and density are easily determined. Hence the molar polarisation in a given field is easily measured.

But from experimental determinations it was soon found that the molar polarisation of many substances like CO_2 , CH_4 , N_2 , etc. remained constant and did not vary with temperature, whereas in other cases such as those of HCl , CH_3Cl , $\text{C}_6\text{H}_5\text{NO}_2$, etc. the molar polarisation was temperature-dependent. This anomaly and difference of behaviour led Debye (1912) to classify the molecules to form into two groups having coincident and non-coincident centres of positive and negative charges as explained in sec VII.5. We shall now examine the effect of the field on polar molecules in which the centres of gravity do not coincide and there is a permanent dipole moment (μ) of the molecule.

VII.7. Permanent Dipole Moment. Each of the polar molecules has a positive and a negative end. Normally in the absence of an electric field, the molecules would be randomly oriented in all directions due to thermal effect. But when such molecules are placed in an electric field between two charged plates, there will arise two distinct effects. Firstly, the usual distortion of the positive and negative charges would occur giving rise to induced polarisation. Secondly, the field would tend to orient all the molecules (since they are polar) in the direction of the field. Had the molecules been stationary these would be oriented at 180° to the direction of the field, the positive ends pointing towards the negative plate. But owing to thermal agitation which opposes such orientation the molecules would occupy some mean position between the direction of the field and their original positions, as in Fig. VII.3 (b). This effect of the field on the molecules is called the *orientation polarisation*, P_o .

The molar polarisation, which is measured from dielectric constant, $\left[\frac{D-1}{D+2} \cdot \frac{M}{\rho} \right]$ is the sum of the two effects, induced and orientation polarisations. That is, the total molar polarisation,

$$P_t = P_i + P_o$$

and

$$P_i = \frac{D-1}{D+2} \cdot \frac{M}{\rho}$$

$$\therefore \frac{D-1}{D+2} \cdot \frac{M}{\rho} = P_t + P_o = \frac{4}{3} \pi N_0 \alpha + P_o \quad \dots \text{(VII.14)}$$

The molar orientation polarisation (P_0) of a substance having a dipole moment (μ) was shown by Debye to be expressed as (see appendix 5.)

$$P_0 = \frac{4}{3} \pi N_0 \left(\frac{\mu^2}{3kT} \right) \quad \dots \text{(VII.15)}$$

This shows that (a) in a non-polar molecule ($\mu = 0$) there is no orientation polarisation and (b) that orientation polarisation is inversely proportional to temperature. We now have,

$$P_t = \frac{D-1}{D+2} \cdot \frac{M}{\rho} = \frac{4}{3} \pi N_0 a + \frac{4}{3} \pi N_0 \left(\frac{\mu^2}{3kT} \right) \quad \dots \text{(VII.16)}$$

Because the first term on the right-hand side is a constant and μ is also constant for a given substance, the relation may be expressed as

$$P_t = \frac{D-1}{D+2} \cdot \frac{M}{\rho} = a + \frac{b}{T} \quad \dots \text{(VII.17)}$$

where

$$a = \frac{4}{3} \pi N_0 a, \text{ and } b = \frac{4\pi N_0}{9k} \mu^2$$

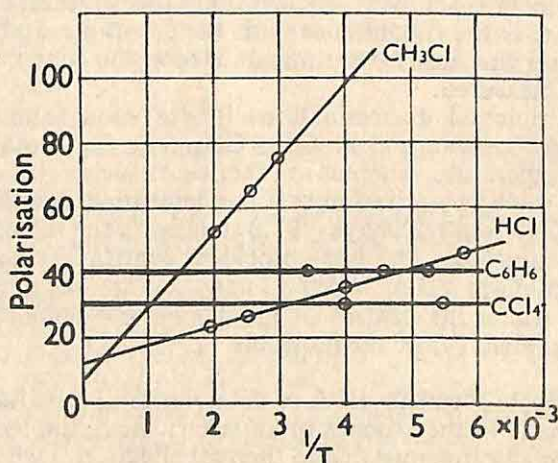


Fig. VII.4

which shows the total molar polarisation will vary linearly with $1/T$. That this is true is amply proved from experiments, as indicated in Fig. VII.4 in which P_t vs $1/T$ are plotted for several substances. The plots in cases of C_6H_6 and CCl_4 are found to be parallel to $1/T$ axis indicating their temperature independence and hence non-polar character. The graphs of CH_3Cl and HCl show that P_t varies linearly with $1/T$. The slopes of these lines give the value of b of equation VII.17 and hence the dipole moment (μ) is known.

VII.8. Determination of Dipole Moment. There are a number of methods for ascertaining the dipole moment. We shall discuss the principle involved in a few of these.

(i) **Temperature Method.** From a direct measurement of the dielectric constant, the total polarisation (P_t) of a substance is obtained, M and ρ being separately determined. We have seen in the previous section,

$$P_t = a + \frac{b}{T}$$

If total polarisation P_1 and P_2 be determined at two temperatures T_1 and T_2 , then

$$b = (P_1 - P_2) \left(\frac{T_1 T_2}{T_2 - T_1} \right)$$

The value of the dipole moment μ is easily calculated from that of b , for,

$$b = \frac{4\pi N_0}{9k} \mu^2$$

$$\text{or } \mu = \sqrt{\frac{9k}{4\pi N_0} b} = 0.0128 \times 10^{-18} \cdot \sqrt{b} \text{ esu.} \quad \dots \text{ (VII.18)}$$

putting the standard values of N_0 , k and π .

[Dipole moment are often expressed in terms of "Debye" units, when 1 Debye unit = 10^{-18} esu of moment.]

(ii) **Ebert's Method.** Polar molecules in gaseous state, if subjected to an electric field, will suffer both orientation as well as distortion polarisation. But if the same substance in solid state be subjected to the field, orientation of molecules is not possible and only distortion polarisation will occur. As such we have for total molar polarisation,

$$P_{gas} = P_t + P_o; \quad P_{solid} = P_t$$

Hence the orientation polarisation, $P_o = P_{gas} - P_{solid}$

$$\text{or } \frac{4\pi N_0}{3} \left(\frac{\mu^2}{3kT} \right) = P_{gas} - P_{solid}$$

$$\text{or } \mu = \sqrt{\frac{9kT}{4\pi N_0} (P_{gas} - P_{solid})}$$

Since the quantities on right-hand side are known, the value of μ is obtained.

(iii) **Refractivity Method.** The induced polarisation, P_t is due to the distortion of the nuclei and of the electrons. If we consider these two distortions separately, we may say

$$P_t = P_a + P_e$$

where P_a , called atom polarisation, represents that due to distortion of the nuclei and P_e , called the electron polarisation, is due to distortion of the electrons. Hence the total polarisation, P_t , is

$$P_t = P_a + P_e + P_o$$

Maxwell showed that for the same electromagnetic wave, the refractive index (n) of a medium is related to its dielectric constant (D) by the expression, $D = n^2$. Hence the total polarisation $\frac{D-1}{D+2} \cdot \frac{M}{\rho}$ seems replaceable by the molar

refraction $\frac{n^2-1}{n^2+2} \cdot \frac{M}{\rho}$. (see eqn. VII.7). But this is not strictly so. The refractive index is measured with visible radiations of higher frequency (say D-line of sodium) whereas the dielectric constant is measured with long waves. The refractive index (n) changes somewhat with wavelength. The correction for refractive index for lower frequency is obtained with the empirical Cauchy formula

$$n = n_\alpha + \frac{a}{\lambda^2}$$

where n = refractive index at wavelength λ and n_α at very high wave-lengths; 'a' is a constant whose value may be ascertained from two measurements of n at known frequencies in the visible region. We shall therefore replace D by n_α^2 .

More important is the fact that in refraction only the electrons are affected by the radiation. Even when corrected for long waves, the refractive index gives the effect of the long-waves on the electrons only. The nuclei remain unaffected. As such, the molar polarisation expressed by

$$\frac{n_a^2 - 1}{n_a^2 + 2} \cdot \frac{M}{\rho}$$

gives only the electron polarisation (P_e) and not the total molar polarisation,

$$\text{or} \quad P_e = \frac{n_a^2 - 1}{n_a^2 + 2} \cdot \frac{M}{\rho}$$

$$\therefore P_t = \frac{D-1}{D+2} \cdot \frac{M}{\rho} = P_a + \frac{n_a^2 - 1}{n_a^2 + 2} \cdot \frac{M}{\rho} + \frac{4\pi N_0}{9kT} \mu^2 \quad \dots \text{(VII.19)}$$

This indeed gives us a method for determination of atom polarisation P_a . μ may be obtained by any of the methods described previously and then if D and n_a^2 be separately measured, their substitution will enable us to evaluate P_a .

It has been found that for relatively large organic molecules, the atomic polarisation P_a is quite small compared to the electronic polarisation, P_e . The former is approximately 5% of the latter. On this assumption, we may write eqn. (VII.19) as

$$\frac{D-1}{D+2} \cdot \frac{M}{\rho} = 1.05 \frac{n_a^2 - 1}{n_a^2 + 2} \cdot \frac{M}{\rho} + \frac{4\pi N_0}{9kT} \mu^2 \quad \dots \text{(VII.20)}$$

In such cases, measurement of dielectric constant and of refractive index would give the value of the dipole moment.

(iv) **Solutions.** The orientation polarisation (P_0), from which the value of dipole moment (μ) is obtained, is evaluated from measurements of dielectric constant in the gaseous state. For substances, which are not easily obtained in gaseous state, solutions in non-polar solvents are used. The total molar polarisation of a solution (P_{12}) in a non-polar solvent like C_6H_6 , CCl_4 , etc. follows the additivity rule and may be expressed as

$$P_{12} = \frac{D-1}{D+2} \cdot \frac{(x_1 M_1 + x_2 M_2)}{\rho}$$

where x_1 , and x_2 are the mol-fractions of solvent and solute. Suffix 1 is used for solvent and suffix 2 for solute. Then,

$$P_{12} = x_1 P_1 + x_2 P_2$$

$$\text{or} \quad \frac{D-1}{D+2} \cdot \frac{x_1 M_1 + x_2 M_2}{\rho} = \frac{D_1-1}{D_1+2} \cdot \frac{M_1}{\rho_1} \cdot x_1 + \frac{D_2-1}{D_2+2} \cdot \frac{M_2}{\rho_2} \cdot x_2$$

P_1 and P_2 are molar polarisation of solvent and solute ; ρ , density of mixture.

The value of P_1 is first separately determined from dielectric-constant measurement of pure solvent. Subsequently, from the determination of dielectric constant of the solution at known values of x_1 and x_2 , the value of P_2 can be obtained. In this way P_2 is measured at different temperatures and the same is plotted against $1/T$, from the slope of which, as usual, the dipole moment μ is evaluated. Some corrections are however necessary sometimes to eliminate the solvent effects, if any.

TABLE : DIPOLE MOMENTS OF SOME SUBSTANCES (DEBYE UNITS)

Substance	Dipole moment	Substance	Dipole moment
$\left. \begin{array}{l} \text{H}_2, \text{O}_2, \text{N}_2, \text{Cl}_2, \\ \text{Br}_2, \text{I}_2, \text{CO}_2, \\ \text{CS}_2, \text{SnCl}_4, \text{SnI}_4 \end{array} \right\}$	-0.0	$\begin{array}{l} \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_2\text{H}_4, \text{C}_2\text{H}_2 \\ \text{CCl}_4, \text{CBr}_4, \text{C}_6\text{H}_6 \\ \text{naphthalene, diphenyl,} \\ \text{cyclo-hexane} \end{array}$	- 0.0
HCl	1.03	CH_3Cl	1.86
HBr	0.78	CH_3Br	1.80
HI	0.38	CH_3I	1.35
H_2O	1.84	alkyl chlorides	2.03
H_2O_2	2.10	methyl alcohol	1.70
NH_3	1.49	methyl amine	1.24
N_2H_4	1.84	acetic acid	1.74
N_2O	0.17	chlorobenzene	1.73
H_2S	1.10	<i>p</i> -dichloro benzene	0.0
HCN	2.90	<i>m</i> -dichlorobenzene	1.72
SO_2	1.63	<i>o</i> -dichlorobenzene	2.50
		nitrobenzene	4.23
PH_3	0.55	<i>p</i> -nitrochlorobenzene	2.83
PCl_2	0.78	<i>m</i> -nitrochlorobenzene	3.73
		<i>o</i> -nitrochlorobenzene	4.64
		aniline	1.56

Example : At 20°C, for water,

The molar polarisation = 74.2 c.c.

The index of refraction = 1.333

and the density = 0.998 gm/c.c.

Calculate the dipole moment of water (neglect atom polarisation).

$$\text{The molar refractivity } R_M = \frac{1.333^2 - 1}{1.333^2 + 2} \cdot \frac{18}{0.998} = 3.7 \text{ c.c.}$$

Now

$$P_t = P_a + P_i + P_o$$

Since

$$P_a = 0, P_o = R_M, \text{ we have}$$

$$P_t = R_M + \frac{4\pi N_0}{9kT} \mu^2$$

i.e.,

$$74.2 = 3.7 + \frac{4 \times \pi \times 6 \times 10^{23}}{9 \times (8.4 \times 10^7 / 6 \times 10^{23}) \times 293} \mu^2$$

whence

$$\mu = 1.8 \times 10^{-18} \text{ esu} = 1.8 \text{ d.}$$

Example : The molar polarisation P of cis-dichloro-ethylene ($M = 97$) at 302°K is 93.13 c.c. and at 403.8°K is 74.35 c.c. Calculate its dipole moment.

Also determine its refractive index if its density be 1.28 gms/c.c. at 302°K, assuming atomic polarisation is 5% of distortion polarisation. [cf. J. Am. chem. Soc. 63,661, 1941.]

Let P_D be the distortion polarisation, $P_D = P_a + P_e$

$$\text{At } 302^\circ\text{K}, \quad P_t = P_D + B/T_1 = 93.13$$

$$\text{At } 403.8^\circ\text{K} \quad P_t = P_D + B/T_2 = 74.35$$

$$\text{Hence } B = \frac{(93.13 - 74.35)}{\left(\frac{1}{302} - \frac{1}{403.8}\right)} = \frac{18.78}{0.00332 - 0.00248} = 22357$$

$$\mu = 0.0128 \sqrt{B} = 0.0128 \sqrt{22357} = 1.91 \text{ debye.}$$

∴

$$P_e = 0.95 P_D$$

Now

$$P_D = 93.13 - B/T_1 = 93.13 - 22357 \times 0.00332 = 18.90$$

But

$$P_e = 0.95 \times 18.90 = 17.955 \text{ c.c.}$$

Hence

We know
$$\frac{n^2-1}{n^2+2} \cdot \frac{M}{D} = P_\epsilon = 17.955$$

or
$$\frac{n^2-1}{n^2+2} = 17.955 \times \frac{1.28}{97} = 0.2366$$

whence
$$n = 1.385$$

VII.9. Polarisation and Molecular Radius. The induced polarisation (P_i) may be used to find out molecular radius. Inserting the known values of Avogadro number and π , we have

$$P_i = \frac{4}{3}\pi N_0 a = 2.54 \times 10^{24} a \quad \dots \text{ (VII.21)}$$

Since the refractive index is close to unity for a gas or vapour, we may write

$$P_i = \frac{D_0-1}{D_0+2} \cdot \frac{M}{\rho} = \frac{D_0-1}{3} \times \frac{M}{\rho} = \frac{D_0-1}{3} \times 22.4 \times 10^3 \text{ c.c., at N.T.P.}$$

Substituting in eqn (VII.21),

$$a = 2.94 \times 10^{-21} (D_0 - 1)$$

Again if a conducting sphere of radius r be placed in an electric field of intensity X , the induced electric moment would be

$$\begin{aligned} \mu_i &= r^3 X \\ \text{Since } \mu_i &= aX, \text{ hence } a = r^3. \\ \therefore r^3 &= 2.94 \times 10^{-21} (D_0 - 1) \end{aligned}$$

It is thus easy to obtain the radius of a spherical molecule from polarisability or dielectric constant. The result will however be approximate in view of the liberal assumptions made. Thus for hydrogen, the radius from dielectric constant relation is $0.92 \text{ \AA}$, while from viscosity measurements it is $1.09 \text{ \AA}$.

Example : Estimate the size of a helium atom if its polarisability is $0.4 \times 10^{-24} \text{ c.c.}$

Since $a = r^3$, where r is the atomic radius, we have

$$r = (0.4 \times 10^{-24})^{\frac{1}{3}} = 0.74 \times 10^{-8} \text{ cm} = 0.74 \text{ \AA}$$

VII.10. Dipole Moment and Structure of Molecules. The determination of dipole moment and its interpretation led to surprisingly important informations about configuration of molecules. Indeed dipole moment has proved a valuable weapon in our attack of structural problems of molecules. We may cite some simple illustrations.

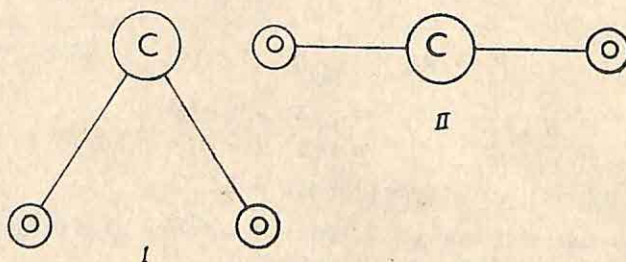


FIG. VII.5

Carbon dioxide has been found to be non-polar, $\mu = 0$. With carbon atom in the middle, this triatomic molecule may either have the triangular structure (I) or the linear structure (II) as in Fig. VII.5. Since the electrons are drawn towards oxygen atoms, the triangular structure would always make the resultant molecule polar, whereas in the linear structure, the electric moment on one side of the carbon atom is counterbalanced by the moment on the opposite, so that the molecule would be non-polar. Hence, carbon dioxide molecule has a linear structure.

On the other hand, the water molecule has an appreciably large dipole moment, which rules out the possibility of its having a symmetrical linear structure. The molecule has a triangular structure, the two OH bonds, meeting at an angle. The electric moment created in one O-H bond does not neutralise that produced by the other.

The non-polar character of molecules like H_2 , Cl_2 , N_2 etc. point to the fact that the bonding electrons are symmetrically placed between the two atoms. In fact, in all non-polar molecules there should be a complete symmetrical distribution of the positive and negative charges. The molecule must have an electrical centre of symmetry.

Thus, we find benzene as a non-polar molecule, which confirms the Kekule structure and that it has a planar configuration with its six hydrogen atom in the same plane. If a part of the hexagon or if the hydrogen atoms were not in the same plane, it is easy to see that the molecule would have been polar.

Similarly, boron trichloride is non-polar which suggests that it has a planar configuration with three chlorine atoms at the corners of an equilateral triangle and boron at the intersection of medians. But PCl_3 or NH_3 molecules have dipole moments. In these molecules, the three halogen or hydrogen atoms are in one plane symmetrically placed in relation to the nitrogen (or phosphorus) atom placed at the apex of a regular pyramid.

Chemical bonding between two atoms is necessarily associated with an electrical moment arising out of the difference in electronegativity of the two atoms. This means that every bond carries with it an electrical moment called the "bond moment". The dipole moment of a molecule is really the vectorial sum of the individual bond moments present in it. To compute the dipole moment then it is necessary to find out the values of various bond moments, such as C-H, O-H, C-Cl etc. No direct method is known to obtain the magnitude of a bond moment. Though not based on a very satisfactory method, the bond moment of a C-H bond has been taken as 0.4d. On this basis analysing the dipole moments of a large number of compounds, Eucken and Meyer prepared a table of moments for different bonds, such as,

H—C	C—Cl	C—O	C=O	H—O	H—N
0.4	1.5	0.7	2.3	1.6	1.3

The bond is directed towards the more electronegative of the two atoms linked.

All saturated hydrocarbons, CH_4 , C_2H_6 , C_3H_8 etc. are found to be non-polar. Let us consider the simplest molecule, methane. Its non-polar character is easily understood from its symmetrical tetrahedral structure with the C-atom at the centre and the four identical valences making an angle of $109^\circ 28'$ with each other. The centre of symmetry is at the nucleus of the C-atom. The absence of dipole moment in the methane molecule implies that any one C-H bond moment exactly counterbalances the net moment contributed (vectorially) by the remaining three C-H bonds i.e., the methyl group as a whole. The CH_3 -group has a regular pyramidal configuration with C-atom at its apex and three hydrogen at the base (fig. VII.6). The resultant moment of the three C-H bonds will be directed along a line from the centre of the base towards the apex and opposite to the fourth C-H bond moment direction. Using symbol m for bond moments, the resultant moment of the CH_3 -group is given by

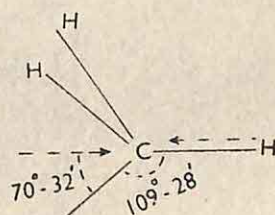


FIG. VII.6

$$m_{CH_3} = 3.m_{CH} \cos (180^\circ - 109^\circ 28') = 3.m_{CH} \times \frac{1}{2} = m$$

That is, the moment of CH_3 -group is the same as that of the C-H bond, i.e., 0.4d. It is obvious that for identical reasons the moment of C_2H_5 or other alkyl group will also be equal to C-H bond moment.

Not only alkyl groups, other groups or radicals such as NH_2 , NO_2 , OH , etc. have definite moments, called group moments. These group moments would naturally depend upon the nature of linkages present in those groups. When one or more of such radicals are present in a molecule, these contribute towards the dipole moment of the same.

It leads to the conclusion that if a hydrogen atom in different saturated hydrocarbons be replaced by OH to produce homologous alcohols, all of the latter should have the same dipole moment. Similarly all alkyl amines, or alkyl chlorides,

would be expected to have identical dipole moment. This is borne out from experimental observations as shown in the table below.

TABLE : DIPOLE MOMENTS (d)

alkyl group	alcohols	amines	chlorides	nitriles
ethyl	1.70	1.3	2.04	3.57
propyl	1.66	1.4	2.04	3.57
Butyl	1.65	1.3	2.04	3.57

The magnitude of the group moments varies slightly in aromatic compounds from those in aliphatic ones. In 1929 Williams computed the following group moments for aromatic compounds :

NO ₂	CHO	OH	Cl	Br	COOH	CH ₃	NH ₂	H
-3.9	-2.8	-1.7	-1.5	-1.5	-0.9	+0.4	+1.5	0.0

[—minus sign indicates the moment directed away from the aromatic ring]

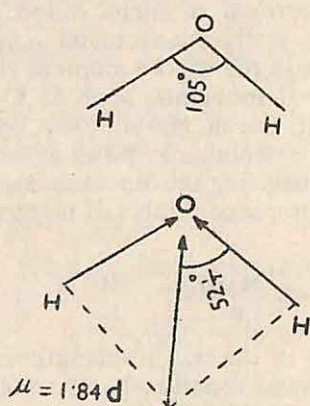


FIG. VII.7

The measured dipole moment of water is 1.84 d and it results from two identical OH bonds each of moment 1.6 d. The resultant as shown in Fig. VII.7 works out to an angle of 105° between the two bonds. This illustrates the application of bond moments and also shows how the dipole moment enables us to determine the bond angles and hence the structure.

Let us take another example. The structure of methyl alcohol is shown in Fig. VII.8, in which the known valence angles have been adopted. The bond moments are $m_{OH} = 1.6$, $m_{C-O} = 0.7$, $m_{CH_3} = m_{CH} = 0.4$. The resultant dipole moment comes out to be 1.56 d while the observed value is 1.65 d, thus conforming to the structure used in calculation.

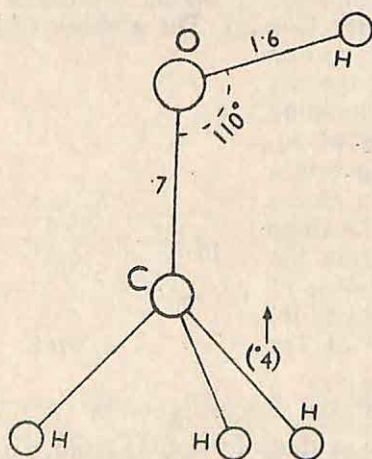


FIG. VII.8(a)

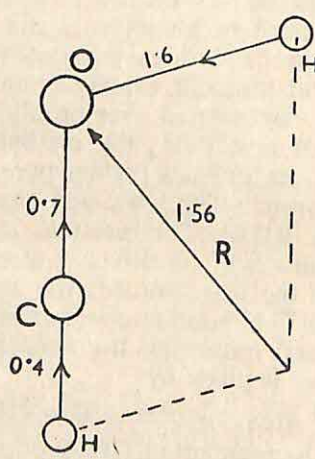


FIG. VII.8(b)

Benzene, which is non-polar, acquires dipole-moment when one of its hydrogen is substituted. Thus, we have,

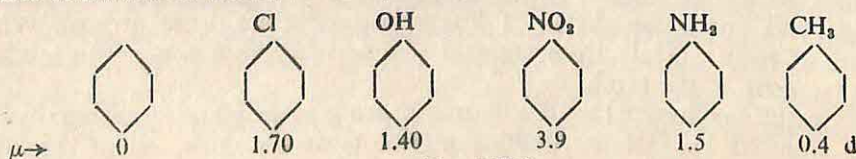


FIG. VII.9

That the vector sums of individual bond or group moments lead to the dipole moment is amply illustrated from a comparison of the calculated and measured dipole moments of many di-substituted benzene derivatives. If m_1 and m_2 be the bond moments and α be the angle between their directions for two substituents of benzene, then

$$\mu = [m_1^2 + m_2^2 + 2m_1m_2\cos \alpha]^{\frac{1}{2}}$$

It is easily seen that $\alpha = 60^\circ$ for ortho, 120° for meta and 180° for para derivatives. The values for some of these compounds are tabulated here.

TABLE : DIPOLE MOMENTS OF $C_6H_4X_1X_2$ COMPOUNDS

X_1	X_2	ortho		meta		para	
		μ_{calc}	μ_{obs}	μ_{calc}	μ_{obs}	μ_{calc}	μ_{obs}
CH ₃	Cl	1.39	1.35	1.79	1.78	1.95	1.90
CH ₃	NO ₂	3.76	3.66	4.16	4.17	4.3	4.4
Cl	NO ₂	5.26	4.60	3.68	3.69	2.52	2.7
NH ₂	NO ₂	3.64	4.26	4.74	4.85	5.17	5.21
Cl	CN	4.88	4.75	3.4	3.4	2.4	2.5

The concordance of the experimental values with the calculated ones is inescapable. In disubstituted ortho compounds, some deviation is often noticed specially when the substituents have strong bond moments. This is due to the inductive and mesomeric effect of the two groups in close proximity.

In the special case when $x_1 = x_2$, i.e., two substituents are identical, we have for ortho, $\mu = \sqrt{3}m_1$; meta $\mu = m_1$, para $\mu = 0$. This is confirmed from the observations that *m*-dinitro benzene and nitrobenzene have same μ -values and that *p*-dinitro, *p*-dimethyl benzenes have all $\mu = 0$.

Further the observation that *p*-dihydroxybenzene, *p*-C₆H₄(OH)₂, has a dipole moment of 1.64 shows that the two O-H links are not in the plane of the ring but inclined to the plane, so that a net moment has resulted.

Ionic Character of Bonding : Consider a simple heteronuclear diatomic molecule like HCl. How the bonding electrons are located and shared between the two atoms can be somewhat assessed from calculations of dipole moment. For HCl, the dipole moment has been found to be 1.04 d and the bond-length, from infra-red spectra, to be 1.275 Å. If we consider the molecule to be composed of two separate ions, hydrogen having been fully deprived of the electrons as Cl⁻-H⁺, then the dipole moment would be

$$\mu = (4.8 \times 10^{-10}) \times (1.275 \times 10^{-8}) \text{ e.s.u.} = 6.1 \text{ debye.}$$

But the measured value is only 1.04 d. If the bonding electrons were symmetrically located between the two nuclei, the dipole moment would have been zero. The ionic character is then expressed as

$$\% \text{ ionic} = \frac{\mu_{obs}}{\mu_{calc}} \times 100 = \frac{1.04}{6.1} \times 100 = 17\%$$

Besides these, the knowledge of dipole moments is quite helpful in the interpretation of behaviour of solutions and gases often different from their ideal states, in the explanation of solubilities and the influence of solvents on reaction rates etc.

F. MOLECULAR SPECTRA

VII.11. Molecular Spectra. Atomic spectra, we have seen, consist of sharp lines which are grouped into series. The frequency of the lines is determined from the

difference in energy between two electronic states of the atom, $\nu = \Delta E/h$. The spectra produced even by simple diatomic molecules are much more complicated. In the early days of investigation, molecular absorption spectra were found as broad continuous bands. Hence molecular spectra were often mentioned as "Band spectra" in distinction from line-spectra of the atoms. But later on, with spectroscopes of high resolving power, the bands were found to consist of innumerable closely-packed lines. The number of lines found even in a diatomic molecule spectra is extraordinarily large. These lines could be classified into groups or closely related series called "Bands", the lines in each band becoming closer and

closer until these merge into an edge called 'band-head'. Again, a large number of bands are found clustered together forming a band-group. These bands are found in three distinct regions of the electromagnetic spectrum, namely (i) the microwave or far infra-red, (ii) the near infra-red and (iii) the visible-ultraviolet regions. Because of the complication involved, it is the spectra of the diatomic and some triatomic molecules which have so far been completely studied. For polyatomic molecules, only partial information could so far be secured. A careful study of these lines lead to most useful knowledge regarding molecular structure and the results are often empirically employed for analysis and identification. The spectra of molecules have yielded information in respect of shape and size of molecules, the bond-distances, the strength of bonds and dissociation energy. The determination of vibration frequencies from the spectra enables us to evaluate the thermodynamic properties of the molecule.

In atomic spectra only the difference in energy of electronic states was involved. But for molecules, we are to consider three types of energy. In addition to the electronic energy, molecules also have energy due to vibration and rotation.* Each one of these energies is quantised and can exist with some discrete values. Whenever there is a change in quantum level in any one or more of these types of

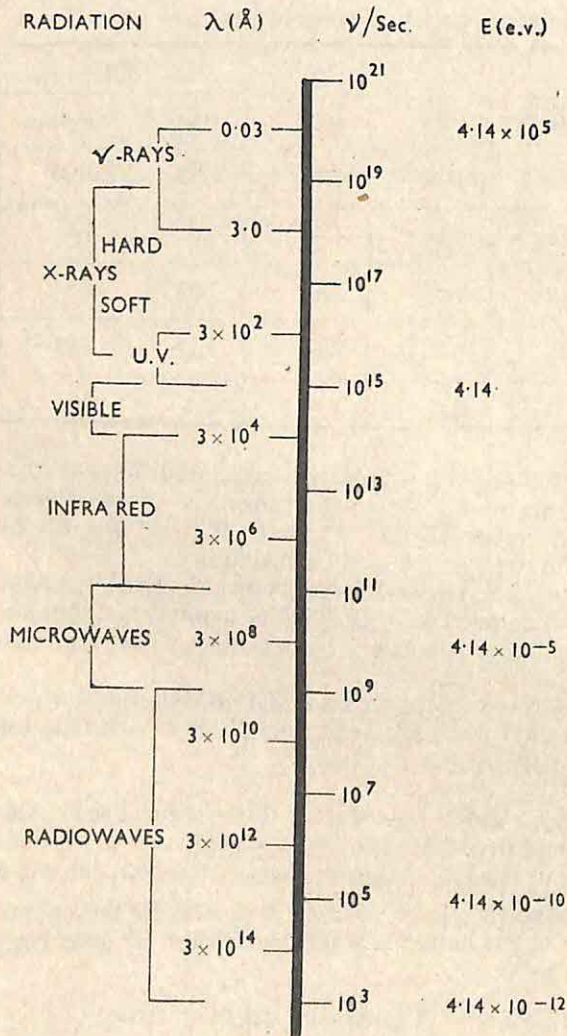


FIG. VII.10

tion to the electronic energy, molecules also have energy due to vibration and rotation.* Each one of these energies is quantised and can exist with some discrete values. Whenever there is a change in quantum level in any one or more of these types of

*In spectroscopy the translational energy is ignored. The possible quantum levels of this energy for a molecule (mass m) in a cube of say l cms side are given by wave-equation as

$$E_{tr} = \frac{h^2}{m} \cdot \frac{1}{8l^2} \left(n_x^2 + n_y^2 + n_z^2 \right),$$

where n_x, n_y, n_z are quantum numbers associated with the momentum of the particle along the three axes. Since h^2/m is of the order of 10^{-20} , the separation of translational levels is too small and the process is regarded as continuous. No separate lines can be found in practice.

energy, there would be absorption or emission of energy. There may be a change only in rotational levels; there may also be a change in vibrational levels on which a rotational change may be superimposed; or an electronic state may change simultaneously with changes in both vibrational and rotational energies. In consequence, even with a simple molecule there is a possibility of a large number of changes in energy states resulting in many spectral lines.

Schemetically, we may visualise the energy states as in the Fig. VII.11. A and B are the two electronic states of a molecule. In each of the electronic states, there are vibrational levels indicated by ν ($=0, 1, 2, 3, \dots$). Again for each vibrational state, there exist several rotational levels indicated by j ($=0, 1, 2, 3, \dots$). A possible transition in any one of these levels will lead to a change in energy content and hence give rise to spectral lines.

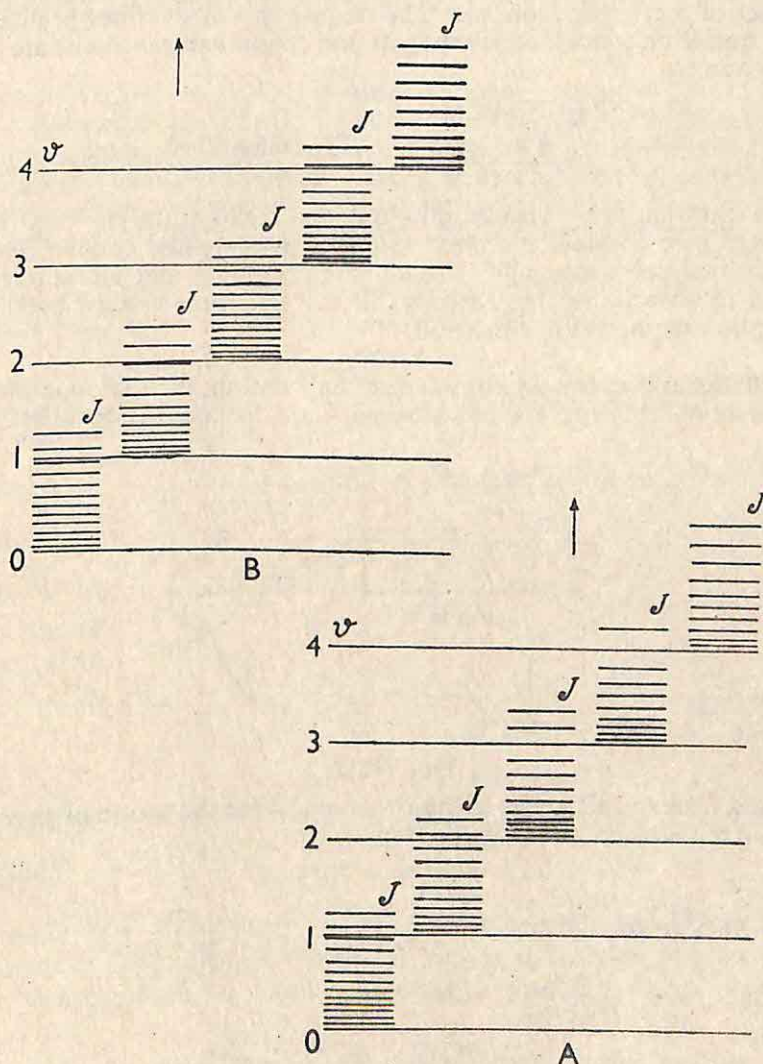


FIG. VII.11

A change in rotational quantum level involves a small energy change of the order of 0.005 e.v. Hence, the frequency ν of the corresponding line in the spectrum would be given by

$$h\nu = 0.005 \times 1.6 \times 10^{-12} \text{ ergs.}$$

$$\text{or } \lambda = c/\nu = \frac{c \times h}{0.005 \times 1.6 \times 10^{-12}} = \frac{3 \times 10^{10} \times 6.6 \times 10^{-27}}{0.005 \times 1.6 \times 10^{-12}} = 2500,000 \text{ \AA} = 250\mu.$$

In other words, the spectral lines appearing in the microwave region are due to pure rotational change. That is, the far infra-red spectrum is the *rotational spectrum*.

In a vibrational quantum level change, the approximate energy-difference per quantum level is of the order of 0.1 e.v., i.e.,

$$\lambda = \frac{c \times h}{0.1 \times 1.6 \times 10^{-12}} = 125000 \text{ \AA} = 12.5 \mu$$

The vibrational spectra would therefore appear in the near infra-red region. During a vibrational change, the rotational energy also changes and the energy emitted or absorbed is the sum of the two energy changes. That is why the near infra red spectrum is called the *vibration-rotation spectrum*.

A change in electronic state is associated with a larger difference in energy of the order of 5 e.v. per molecule. The frequency ν of the lines produced from electronic transition (on which vibrational and rotational transitions are superimposed) is given by

$$h\nu = 5 \times 1.6 \times 10^{-12}$$

$$\text{i.e., } \lambda = \frac{h \times c}{5 \times 1.6 \times 10^{-12}} = \frac{3 \times 10^{10} \times 6.6 \times 10^{-27}}{8 \times 10^{-12}} = 2500 \text{ \AA} = 0.25 \mu.$$

Hence, the spectrum in the visible and ultraviolet region is the *electronic spectrum*.

We shall now consider the three spectra separately and confine our interest to diatomic molecules generally. Usually the rotational and vibrational spectra are studied in absorption spectroscopy. In the electronic spectra both emission and absorption methods are employed.

VII.12. Rotational Spectra. In considering the rotation, the diatomic molecule is regarded as a rigid rotator. The two atoms are at a distance r (Fig. VII.12).

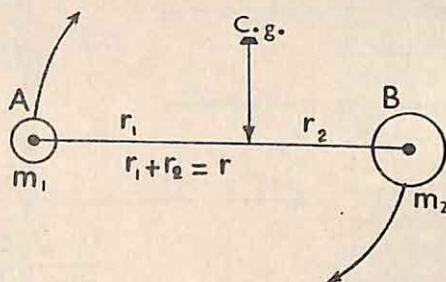


FIG. VII.12

If r_1 and r_2 be the distances of the two atoms from the centre of gravity of the system, then the moment of inertia (I) is given by

$$I = m_1 r_1^2 + m_2 r_2^2$$

We know, $m_1 r_1 = m_2 r_2$, hence $r_1 = \frac{m_2}{m_1 + m_2} r$, $r_2 = \frac{m_1}{m_1 + m_2} r$

Substituting, $I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$

where the reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$. The kinetic energy of rotation is

$$E_{rot} = \frac{1}{2} m v^2 = \frac{1}{2} m r^2 \left(\frac{v}{r} \right)^2 = \frac{1}{2} I \omega^2$$

where angular velocity $\omega = v/r$.

Since the molecule is rigid, the potential energy $V = 0$. The quantised energy levels of rotation are obtained by solving the Schrödinger equation,

$$\nabla^2 \psi + \frac{8\pi^2 \mu E}{h^2} \psi = 0$$

The appropriate and acceptable solutions of this equation show that

$$E = \frac{h^2}{8\pi^2 I} j(j+1) \quad \dots \text{(VII.22)}$$

where j is the rotational quantum number having integral values 0, 1, 2, 3, ...

For a given species of molecules, $\frac{h^2}{8\pi^2 I}$ is a constant which is substituted by B , called the rotational constant. So,

$$E = Bhj(j+1) \quad \dots \text{(VII.23)}$$

The difference in energy between two rotational levels j and j' ,

$$\Delta E = Bhj(j+1) - Bhj'(j'+1) \quad \dots \text{(VII.24)}$$

There are however two restrictions in such rotational transitions.

I. As predicted from electrodynamic considerations the absorption or emission of radiation in rotational levels would occur only if a change in dipole moment of the molecule is associated with it. That is, the molecule must be polar in order to produce a rotational spectrum. Homopolar molecules like H_2 , N_2 , Cl_2 , ... etc. have no rotational band. This restriction also applies to vibrational quantum level changes.

II. The transition in rotational energy is limited to adjacent levels, i.e., $\Delta j = \pm 1$. Since $j - j' = 1$, equation (VII.24) takes the form

$$\Delta E = Bhj(j+1) - Bh(j-1)j = 2Bhj \quad \dots \text{(VII.25)}$$

where higher quantum level $j = 1, 2, 3, \dots$; j cannot be zero. For in that case j' becomes negative. Now $\Delta E = h\nu$, $\therefore \nu = 2Bj$

Putting $j = 1, 2, 3, \dots$, the frequencies of the lines in the rotational band are

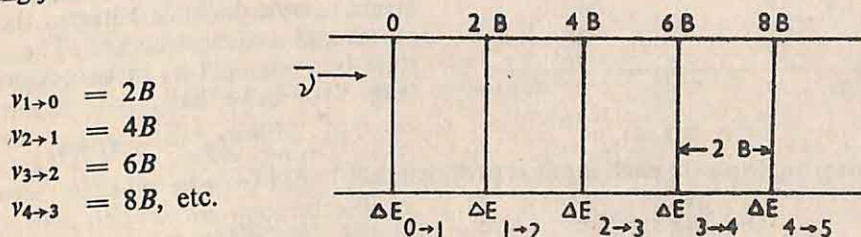


FIG. VII.13

The spectral lines are thus equispaced, the spacings $\Delta \nu = 2B$. The difference in wave numbers $\Delta \bar{\nu} = \frac{\Delta \nu}{c} = \frac{2B}{c}$.

The equidistant lines have been experimentally confirmed (Fig. VII.13) and the magnitude of B ascertained. Thus, for hydrogen chloride, the wave number difference between successive lines has been found to be 20.3, i.e.,

$$\Delta \bar{\nu} = 20.3, \quad \text{or} \quad \frac{2h}{8\pi^2 Ic} = 20.3$$

whence

$$I_{HCl} = 2.7 \times 10^{-40} \text{ gm-cm}^2$$

Again for HCl,

$$H = 1.008, \text{ Cl} = 35.46, \text{ and } N_0 = \text{Avo. number}$$

$$\therefore \mu = \frac{(m_1 \times m_2)/N_0}{(m_1 + m_2)/N_0} = \frac{1.008 \times 35.46}{36.468 \times 6.023 \times 10^{23}} = 1.63 \times 10^{-24} \text{ gms}$$

Hence, the bond-distance $r = \sqrt{I/\mu} = \sqrt{(2.7 \times 10^{-40})/(1.63 \times 10^{-24})} = 1.29 \text{ \AA}$

This indeed is the most accurate determination of bond distance. We also

know the rotational energy at any level and the moment of inertia of the molecule. Some bond distances from microwave spectroscopy are tabulated below :

TABLE

molecule	$I \times 10^{40}$	r (Å)
HCl	2.65	1.29
HBr	3.31	1.41
HI	4.29	1.60
NO	16.5	1.15
CO	14.5	1.13

It should be mentioned here that at higher quantum levels of rotation when the speed is quite large, the rigid character of the rotator is affected and there is a tendency for the bond to stretch. The energy of rotation is then expressed as

$$E_{rot} = Bhj(j+1) - Dhj^2(j+1)^2 \quad \dots (VII.26)$$

where D is a small constant of the order of $10^{-4}B$. The spectral lines will not then be exactly equidistant especially at higher levels.

Linear triatomic polar molecules like COS, HCN etc. behave exactly like HCl-molecule in their rotational transitions. In fact, equispaced lines were observed in the microwave absorption spectra, from which B and I were obtained.

VII.13. Vibration-Rotation Spectra. We have seen that the vibration spectra appear in the near infra-red region as the energy-changes in vibrational transitions are

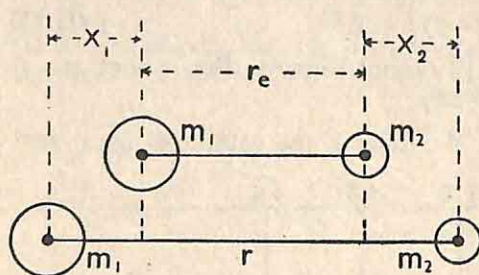


FIG. VII.14

larger than those in rotational transitions. In a diatomic molecule, two atoms A and B , having masses m_1 and m_2 oscillate against one another. The idealised vibration may be assumed to be a harmonic one. Let r_e be the equilibrium atomic distance between the two atoms and r when stretched. The atoms shift by $-x_1$ and x_2 in two directions (Fig. VII.14), so that

$$x = r - r_e = -x_1 + x_2$$

The restoring force on each atom is proportional to x , i.e.,

$$m_1 \frac{d^2x}{dt^2} = kx \quad \text{and} \quad m_2 \frac{d^2x}{dt^2} = -kx$$

where k is the force constant.

$$\frac{d^2x}{dt^2} = \frac{d^2(x_2 - x_1)}{dt^2} = -kx \left(\frac{1}{m_1} + \frac{1}{m_2} \right) = -\frac{kx}{\mu}$$

Solving :
$$x = A \sin \left(t \sqrt{\frac{k}{\mu}} + c \right)$$

The general equation of the harmonic motion is $x = A \sin (2\pi wt + c)$, where w is the frequency of vibration.

So,
$$2\pi\omega = \sqrt{\frac{k}{\mu}} \quad \text{or} \quad \omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \dots (VII.27)$$

Again, the restoring force is related to the potential energy (V) as

$$F = -\frac{\partial V}{\partial x} \quad \text{or} \quad V = \frac{1}{2}kx^2$$

The vibrational energy levels may now be determined from Schrödinger equation [only x -direction of oscillation being considered].

$$\nabla^2 \psi + \frac{8\pi^2\mu}{h^2} [E - \frac{1}{2}kx^2] \psi = 0.$$

The allowed solutions of this equation are given by

$$E_{vib} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \cdot (v + \frac{1}{2}) = (v + \frac{1}{2}) h\omega \quad \dots (VII.28)$$

where v has integral values 0, 1, 2, 3, ... indicating the vibrational quantum numbers. It should be realised that even at the ground state ($v = 0$), the molecule would have vibrational energy $\frac{1}{2} h\omega$, called the zero-point energy.

The infra-red spectra are usually studied in absorption. In a vibrational transition from quantum level v to v' the energy-change is (eqn. VII.28).

$$\Delta E = (v' - v) h\omega \quad \dots (VII.29)$$

If the transition is restricted to adjacent quantum levels (selection principle), then $\Delta v = v' - v = 1$, or $\Delta E = h\omega$.

Hence

$$h\nu = h\omega, \text{ or } \nu = \omega$$

i.e., ν , the frequency of the absorbed radiation is the same as the fundamental frequency of vibration (ω) of the molecule. It follows that for any vibrational transition between adjacent levels (e.g., $0 \rightarrow 1$, $2 \rightarrow 3$, $5 \rightarrow 6$, ...) only one spectral line would appear, ($\nu = \omega$), in the near infra-red spectra. But the infra-red spectra really consist of a number of bands each with a fine structure. To understand this, it is necessary to take into account two other facts of vital importance.

I. Only at their lowest states of vibration, the diatomic molecules behave fairly closely as simple harmonic oscillators. But at higher quantum levels there is a departure and the vibrations become anharmonic. As such the vibrational energy would more properly be expressed as

$$E_{vib} = (v + \frac{1}{2}) h\omega - (v + \frac{1}{2})^2 h\omega x \quad \dots (VII.30)$$

where x is called the anharmonicity constant and has a small magnitude.

This departure from harmonic oscillations may be graphically illustrated, (as in Fig. VII.15) by the observed potential energy curves and the vibrational energies calculated on assumption of simple harmonic character. The energies are plotted against atomic distances. The theoretical curve is truly parabolic while the observed one (dotted line) is such only at low quantum levels.

Because of anharmonicity, vibrational transitions are not confined to adjacent levels only, but may also occur between different levels, so that $\Delta v = v' - v = 2, 3, \dots$ etc. As such, from equation (VII.30),

$$\Delta E_{vib} = (v' - v) h\omega - (v' - v)(v' + v + 1) h\omega x$$

We can now express the frequencies of lines from different transitions as in the following :

Transitional levels	Energy changes	Frequencies
$v = 0 \rightarrow v' = 1$	$\Delta E = h\nu_{0 \rightarrow 1} = h\omega(1 - 2x)$	$\nu_{1 \rightarrow 0} = (1 - 2x)\omega$
$v = 0 \rightarrow v' = 2$	$\Delta E = h\nu_{0 \rightarrow 2} = 2h\omega(1 - 3x)$	$\nu_{2 \rightarrow 0} = (1 - 3x)2\omega$
$v = 0 \rightarrow v' = 3$	$\Delta E = h\nu_{0 \rightarrow 3} = 3h\omega(1 - 4x)$	$\nu_{3 \rightarrow 0} = (1 - 4x)3\omega$
$v = 1 \rightarrow v' = 2$	$\Delta E = h\nu_{1 \rightarrow 2} = h\omega(1 - 4x)$	$\nu_{2 \rightarrow 1} = (1 - 4x)\omega$

... (VII.31)

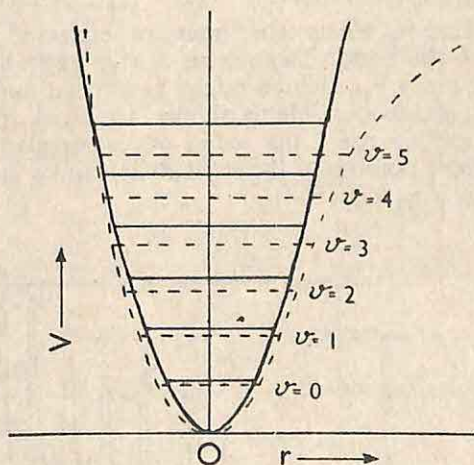


FIG. VII.15

Each different vibrational transition will lead to a separate line in the spectrum with frequencies as indicated above. But this is not enough ; to explain much greater multiplicity we have to consider also another aspect.

II. Pure vibrational transition without affecting rotation is not permitted. A transition in vibration is invariably associated with a rotational transition. In other words, a rotational energy-change is superimposed on the vibrational energy-change. The net change in energy is the algebraic sum of the rotational and vibrational energy-changes,

$$\Delta E = \Delta E_{vib} + \Delta E_{rot}$$

If we consider the vibrational transition $v = 0$ to $v' = 1$, we have from equations (VII.31 and VII.25),

$$\Delta E = h\omega(1-2x) \pm 2Bhj \quad \dots (VII.32)$$

the rotational energy being always governed by selection restriction $\Delta j = \pm 1$, i.e., j may increase or decrease by unity only.

Neglecting anharmonicity factor x , we have, $\Delta E = h\omega \pm 2Bhj$

Now consider the vibration transition, $\Delta v = 1$, say from $0 \rightarrow 1$.

For $\Delta v = 1$, with $\Delta j = 1$ and $\Delta j = -1$, the energy differences are :

$$\Delta E = hv_{0 \rightarrow 1} + 2Bhj \text{ and } \Delta E = hv_{0 \rightarrow 1} - 2Bhj$$

The frequencies of the spectral lines are obtained by putting $j = 1, 2, 3$, etc.

<i>R</i> -branch	<i>P</i> -branch
$\nu_R = \nu_{0 \rightarrow 1} + 2B$	$\nu_P = \nu_{0 \rightarrow 1} - 2B$
$\nu'_R = \nu_{0 \rightarrow 1} + 4B$	$\nu'_P = \nu_{0 \rightarrow 1} - 4B$
$\nu''_R = \nu_{0 \rightarrow 1} + 6B$	$\nu''_P = \nu_{0 \rightarrow 1} - 6B$
$\nu'''_R = \nu_{0 \rightarrow 1} + 8B$	$\nu'''_P = \nu_{0 \rightarrow 1} - 8B$

This predicts that for each vibrational transition there would be two sets of equi-spaced lines in the spectra ; one set called *R*-branch in which frequencies increase uniformly by $2B$ and in the other set called *P*-branch frequencies decrease uniformly by $2B$. There would appear no line at $\nu_{0 \rightarrow 1}$ corresponding to pure vibration ($\Delta j = 0$). The spacing between the first line of the *R*-branch and the first line of the *P*-branch is $\Delta \nu = (\nu_{0 \rightarrow 1} + 2B) - (\nu_{0 \rightarrow 1} - 2B) = 4B$.

That is, when other lines are separated by $2B$, there would be a gap at the centre of the band. The centre of this gap (where no line appears) corresponds to frequency $\nu_{0 \rightarrow 1}$ which might have been due to pure vibration. By locating the centre it is thus possible to obtain the values of both $\nu_{0 \rightarrow 1}$ and B . If the anharmonic relation be used, the value of x can also be found out. The experimental results have confirmed these facts, as shown in the fine structure bands of HCl molecule in Fig. VII.16.

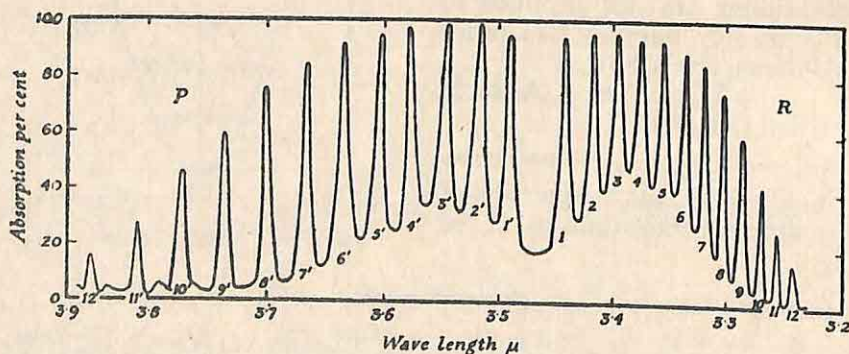


FIG. VII.16 Vibration-rotation spectra (HCl)

Similar results will also be obtained when we consider vibrational transitions $v = 0$ to $v = 2$, or $v = 0$ to $v = 3$ etc. The spectra corresponding to $\Delta v = 1$ are called fundamental bands and others for $\Delta v = 2, 3$ etc. which are less prominent are called overtones. The formation of large number of bands with their fine structure is thus explained.

The frequencies of the origins (ν_0) of the fundamental and overtone bands would be in the ratio (eqn. VII.31),

$$\nu_{1 \rightarrow 0} : \nu_{2 \rightarrow 0} : \nu_{3 \rightarrow 0} = (1-2x)\omega : (1-3x)2\omega : (1-4x)3\omega \approx 1 : 2 : 3,$$

when x is very small.

The experimental values for HCl confirm the expectation,

$$\frac{\Delta \nu_{\text{HCl}}}{\bar{\nu}(\text{cm})^{-1}} \quad \begin{array}{ccc} 0 \rightarrow 1 & 0 \rightarrow 2 & 0 \rightarrow 3 \\ 2886 & 5668 & 8347 \end{array}$$

Hence, the value of the fundamental frequency,

$$\omega = \nu_{0 \rightarrow 1} = 2886 \times 2.99 \times 10^{10} = 8.64 \times 10^{13} \text{ per sec.}$$

[It may be mentioned that the non-rigidity factor has not been taken into account. In fact during a vibrational change, there would be a stretching of the molecule leading to a change in moment of inertia I and in B . These fine corrections have not been introduced in the treatment above.]

VII.14. Force Constant and Amplitude of Vibration. In equation (VII.27),

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \therefore k = 4\pi^2 \omega^2 \mu \quad \dots \text{(VII.33)}$$

The value of ω , the fundamental frequency of vibration, is known from the centre of the fundamental absorption band, $\nu = 0$ to $\nu' = 1$. Hence, the force constant (k) which is a measure of the restoring force with which the molecules are pulled back towards eqm. position is known.

Illustrations : (a) The wave number of the centre of the fundamental band for CO is 2140 cm^{-1} . Hence its frequency is $\nu = 2140 \times 2.99 \times 10^{10} = 6.4 \times 10^{13} \text{ per sec.}$

$\therefore$ Force constant, $k = 4\pi^2 \omega^2 \mu = 4 \times 9.87 \times (6.4 \times 10^{13})^2 \times 1.14 \times 10^{-23} = 18.4 \times 10^5 \text{ dynes/cm.}$
(since $\mu_{\text{CO}} = 1.14 \times 10^{-23}$)

(b) At the ground state ($\nu = 0$), the vibrational energy,

$$E_0 = \frac{1}{2} h\omega = \frac{1}{2} \cdot \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

When the atoms are at their furthest extremities displacement $x = x_{\text{max}}$, the whole of vibrational energy is potential, (E_k is nil), so $E_0 = E_{\text{pot}} = \frac{1}{2} kx^2$

$$\therefore \frac{1}{2} kx^2 = \frac{1}{2} \cdot \frac{h}{2\pi} \cdot \sqrt{\frac{k}{\mu}}$$

$$\text{or} \quad x_{\text{max}} = \left[\frac{h}{2\pi \sqrt{k\mu}} \right]^{\frac{1}{2}} \quad \dots \text{(VII.34)}$$

The amplitude of vibration is thus known. Putting the corresponding values of k and μ for CO, we have $x = 0.05 \times 10^{-8} \text{ cms.}$ [$h = 6.6 \times 10^{-27} \text{ ergs-sec}$]

We have seen (Sec. VII.12), the bond-length of CO is $1.13 \text{ \AA}$. Hence the amplitude is less than 5% of the eqm. bond distance in the ground state.

(c) In H-Cl infra-red spectra, the centre of the fundamental band ($\nu_{0 \rightarrow 1}$) has a frequency $\nu = 8.66 \times 10^{13} \text{ per sec}$ and $\mu = 1.63 \times 10^{-24} \text{ gms.}$

$$\therefore k = 4\pi^2 \omega^2 \mu = 4.98 \times 10^5 \text{ dynes/cm.}$$

The amplitude of oscillation is derived from $\frac{1}{2} kx^2 = \frac{1}{2} \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$

whence $x = 0.12 \times 10^{-8} \text{ cms} = 0.12 \text{ \AA}$

The constants for a few bonds are given below.

Bond	$k \times 10^{-5} \text{ dynes/cm}$	Bond	$k \times 10^{-5} \text{ dynes/cm}$
C—C	4.6	H—Cl	4.8
C=C	9.5	H—Br	4.1
C≡C	15.8	H—I	3.2
C—O	4.9	H—O	7.8 (H ₂ O)
C=O	12.3	C—H	5.9 (C ₂ H ₆)
C≡O	18.6	C—Cl	3.4 (CH ₃ Cl)

VII.15. Isotope Effect. Molecules having different isotopes of the same element, such as DCl and HCl, show different spectra. This is expected, for, the masses of the atoms are different and hence reduced mass as also the frequencies of vibration and of rotation would be different. The atomic distance and the force constant which depend upon the extra nuclear electrons mainly are assumed to remain constant. Indicating the two species of isotopic molecules by suffixes I and II, we have $k = 4\pi^2\omega_I^2\mu_I$ and $k = 4\pi^2\omega_{II}^2\mu_{II}$.

$$\therefore \frac{\omega_I^2}{\omega_{II}^2} = \frac{\mu_{II}}{\mu_I} = \rho^2 \text{ (say)} \quad \dots \text{ (VII.35)}$$

The vibrational frequency of lighter species will be somewhat larger than that of the heavier one. Assuming harmonic vibrations for each species for simplicity, the energy levels of the two species are,

$$\begin{aligned} E_I &= h\omega_I \left(v + \frac{1}{2}\right) \pm 2Bhj, \\ E_{II} &= h\omega_{II} \left(v + \frac{1}{2}\right) \pm 2B'hj \\ \text{i.e., } v_I &= \omega_I \pm 2Bj \\ v_{II} &= \omega_{II} \pm 2B'j \end{aligned}$$

for the same change of vibrational level, $\Delta v = 1$.

Since moment of inertia (I) would be different, the values of 'B' would also change. In consequence, the two species would give two superimposed bands with their origins slightly shifted from one another and the lines in fine structure would appear in duplets. Such double lines have been experimentally established and the isotopic shifts in the lines measured. Hence from equation (VII.35), we have for H^{35}Cl and H^{37}Cl ,

$$\frac{v_I}{v_{II}} = \rho \quad \text{or} \quad \frac{\Delta v}{v_{II}} = 1 - \rho = 1 - \sqrt{\mu_{II}/\mu_I} = 7 \times 10^{-4}$$

$$\text{or} \quad \frac{\delta\lambda}{\lambda} = -7 \times 10^{-4}$$

Knowing λ from spectroscopic measurements with H^{35}Cl , the shift $\delta\lambda$ was calculated and found to be $26.6\text{\AA}$. Lewis and Randall's experimental measurement showed $\Delta\lambda = 25 \pm 2\text{\AA}$.

VII.16. Potential Energy Curves. When the two atoms in a diatomic molecule oscillate against one another, the potential energy (E_v) changes with displacement x . In a harmonic vibration, $x = A \sin(2\pi\omega t + c)$ and the force constant $f = 4\pi^2\omega^2\mu$.

Hence, the vibrational energy = kinetic energy + potential energy

$$\begin{aligned} &= \frac{1}{2}\mu \left(\frac{\partial x}{\partial t}\right)^2 + \frac{1}{2}fx^2 \\ &= \frac{1}{2}\mu \cdot 4\pi^2\omega^2 A^2 \cos^2(2\pi\omega t + c) + \frac{1}{2} \cdot 4\pi^2\omega^2 \mu A^2 \sin^2(2\pi\omega t + c) \\ &= 2\pi^2\omega^2 A^2 \mu \text{ (constant)} \end{aligned}$$

Thus, for a harmonic oscillator the potential energy plotted against interatomic distance should be a parabola and the quantum levels of vibration should be equispaced, $\Delta E_{vib} = h\omega$. But because of anharmonicity the potential energy curve obtained usually is as represented in Fig. VII.17, only at lower quantum levels does it approximate to the parabolic form.

The curve shows that when the two atoms are at considerable distance, the interaction between the atoms is negligible. If the two atoms are brought closer together, an attractive force between the two appears and the potential energy begins to diminish. The two atoms would have finally coalesced, had there not been a repulsive force also when the atoms are sufficiently near. This force of repulsion slowly increases, as the interatomic distance continues to diminish, counterbalancing the attraction. The result is that the potential energy passes through a minimum at M and then sharply rises as the distance between the atoms further diminishes. At the minimum M , the attractive and repulsive forces are equal and the system is expected to be stable. The atomic separation at M , is the equilibrium distance (r_e) between the atoms. But at M , the system has sufficient kinetic energy to

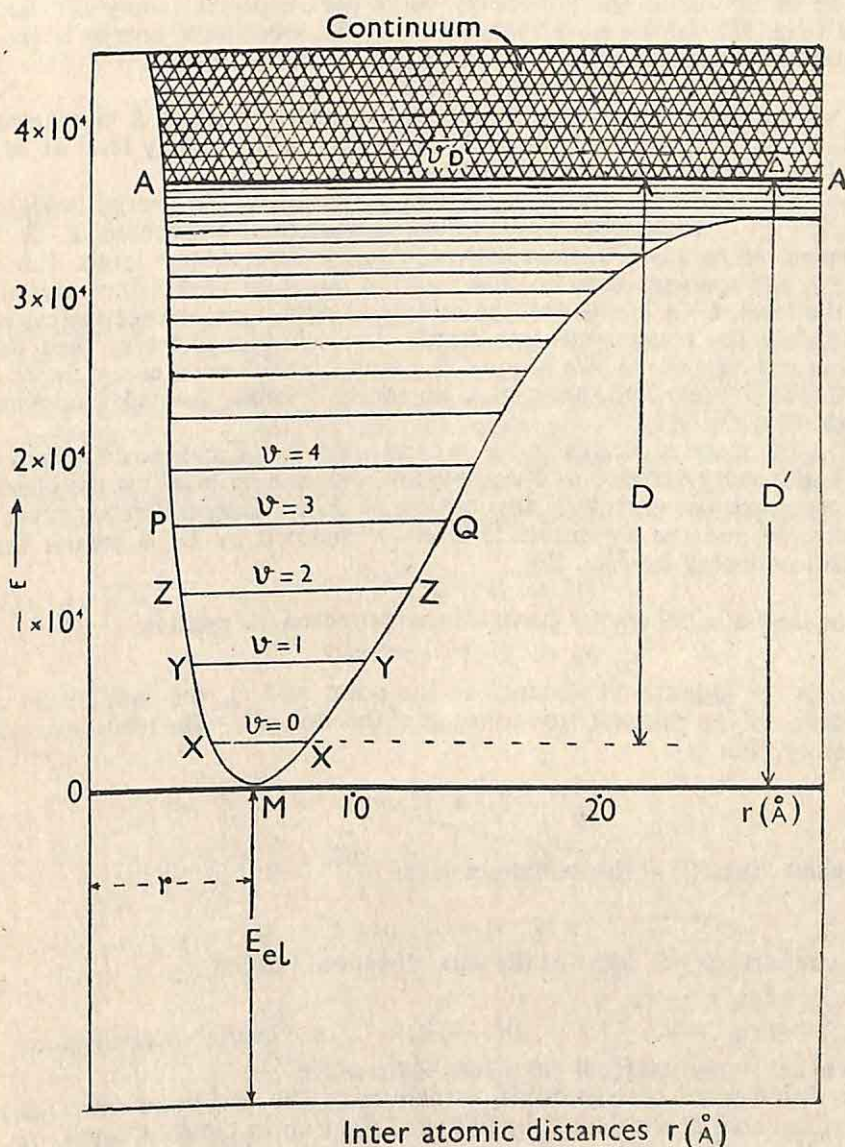


FIG. VII.17

bring the atoms still closer, until E becomes zero when the entire energy is potential. The atoms now recede; the atomic separation increasing and going through the equilibrium reaches the other extreme when again the kinetic energy becomes nil. Thus, for an oscillation PQ , as the atomic distance changes along the horizontal PQ , the potential energy changes along PMQ . The nature of the curve shows that the resistance to compression of the molecule is much greater than that to expansion. As r increases, the curve finally approaches a horizontal asymptote, $r \rightarrow \infty$. This means that when the atomic separation is sufficiently large, dissociation of the molecule would occur.

The total energy E of a diatomic molecule consists of four different types of energy, namely electronic, E_{el} , vibrational E_{vib} , rotational E_{rot} and translational E_{tr} .

That is,

$$E = E_{el} + E_{vib} + E_{rot} + E_{tr}$$

At absolute zero ($T = 0$), E_{rot} and E_{tr} would vanish and hence $E = E_{el} + E_{vib}$

The minimum of the pot-energy curve (M), represents only the electronic energy (Fig. 17). In the ground state $X-X$, the vibrational energy is $\frac{1}{2}h\omega_0$. So, the energy of the system (at $T = 0$) in the ground state

$$E = E_{el} + \frac{1}{2}h\omega_0. \quad \dots (VII.36)$$

Since we are now considering the vibrational energy only in a given electronic state (i.e., E_{el} constant), we may arbitrarily choose the energy level at M to be zero by transposing the reference point.

As the vibrational quantum number is increased the energy levels rise to $Y-Y$, $Z-Z \dots$ horizontals. The spacings between these horizontals $X-X$, $Y-Y$, etc. depend on energy difference between consecutive quantum levels. For anharmonicity, the spacings become closer as the quantum level v increases. Finally when the level $A-A$ is reached, the molecular vibrations become violent enough to dissociate the system into two atoms. The vibrational energy then becomes the kinetic energy of the two atoms. The translational kinetic energy levels are so close that a discrete line spectrum is no longer feasible. Instead a continuum is obtained (Fig. VII.17).

The difference in energy in the ground state $X-X$ and the dissociation level $A-A$ is the energy needed to dissociate the molecule by breaking the bond. This is the spectroscopic energy of dissociation D . The energy-difference between the minimum M and the asymptote level $A-A$ denoted by D' is greater than the dissociation energy by $\frac{1}{2}h\omega$. So,

$$D' = D + \frac{1}{2}h\omega \quad \dots (VII.37)$$

For the potential energy curve, Morse proposed the relation,

$$E_v = D [1 - e^{-a(r-r_e)}]^2,$$

where r is the interatomic distance at the point and r_e , the equilibrium atomic separation, ' a ' is a characteristic constant of the molecule. The relation is evidently satisfactory. For

$$\frac{dE_v}{dr} = 2D.a. [1 - e^{-a(r-r_e)}] [e^{-a(r-r_e)}]$$

which shows that (i) at the minimum when $\frac{dE_v}{dr} = 0$,

$$e^{-a(r-r_e)} = 1, \text{ i.e., } r = r_e.$$

That is, minimum will occur at the eqm. distance. Further,

$$(ii) \text{ when } r = r_e, E_v = 0$$

$$(iii) \text{ when } r \rightarrow \infty, E_v = D(1-0)^2 = D, \text{ the energy of dissociation.}$$

All these are supported from the nature of the curve.

It would have been possible to determine the energy of dissociation (D) if the vibrational spectra could be followed right up to the continuum, but this is not usually possible. Birge and Sponer introduced a method for evaluation of D from energy-difference between consecutive quantum levels (vide equation VII.30),

$$\frac{dE}{dv} = h\omega - 2h\omega x (v + \frac{1}{2})$$

At the asymptote level $A-A$, the quantum levels almost coalesce, i.e., $\frac{\partial E}{\partial v} = 0$.

Indicating this quantum level by v_D , we have

$$2h\omega x (v_D + \frac{1}{2}) = h\omega \quad \text{or} \quad v_D + \frac{1}{2} = \frac{1}{2x}. \quad \dots (VII.39)$$

So, at the dissociation quantum level (v_D)

$$\begin{aligned} E_0 &= D' = (v_D + \frac{1}{2})h\omega - (v_D + \frac{1}{2})^2 h\omega x \\ &= \frac{h\omega}{2x} - h\omega x \cdot \frac{1}{4x^2} = \frac{h\omega}{4x} \end{aligned}$$

$$\therefore \text{The heat of dissociation } D = D' - \frac{1}{2}h\omega = \frac{h\omega}{4x} - \frac{1}{2}h\omega.$$

The spectroscopic determination of ω and x would enable us to evaluate D . Again, at low quantum levels, where anharmonic character is almost absent, expanding eqn, VII.38, we find,

$$E_v = D \left[1 - \frac{a(r-r_e)}{L} - \frac{a^2(r-r_e)^2}{L^2} + \dots \right]^2 \approx Da^2(r-r_e)^2$$

But $E_v = \frac{1}{2}fx^2 = \frac{1}{2} \cdot 4\pi^2\omega^2\mu \cdot (r-r_e)^2$

Comparing $Da^2 = 2\pi^2\omega^2\mu$,

$$a = \pi\omega \sqrt{\frac{2\mu}{D}} \quad \dots \text{ (VII.40)}$$

Hence the constant 'a' is also found out.

For every electronic state of a molecule there is a different and independent potential energy curve. The greater the electronic energy of the molecule the greater is the potential energy. In Fig. VII.18 are shown the potential energy curves at two electronic states, normal (A) and an excited state (B) with their respective vibrational levels. The vertical separation between the zero vibrational levels of the two states A and B indicates the difference in energy ΔE of the two electronic states. The equilibrium interatomic distances (r_e) in the two states are different.

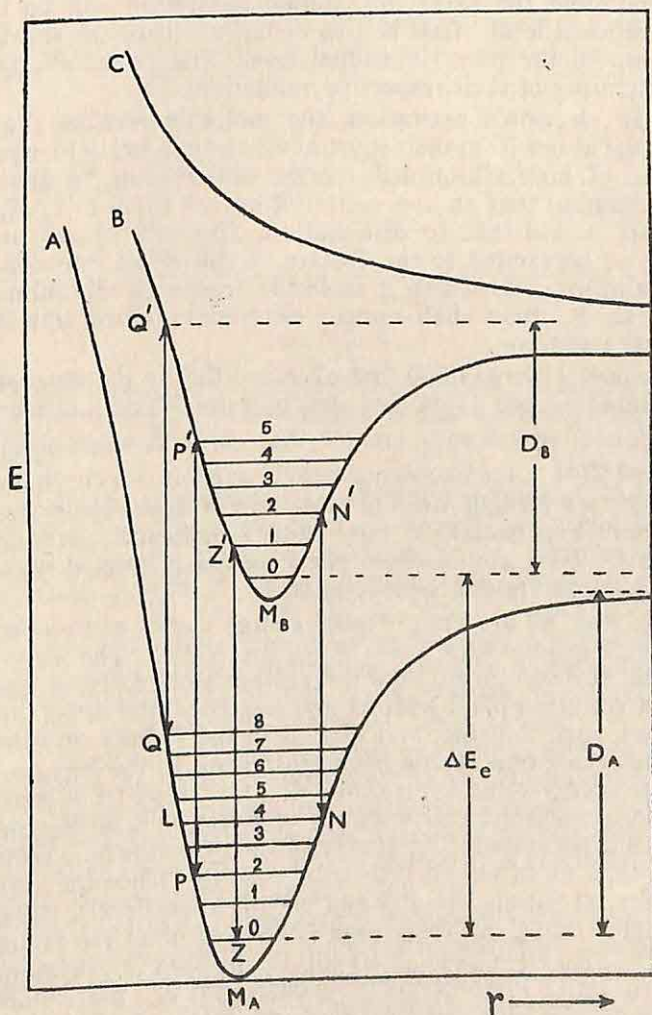


FIG. VII.18 Potential energy curves at lower electronic state (A) and upper electronic states (B & C) showing also a number of Franck-Condon transitions.

It is also found that at higher electronic levels, the energy necessary for dissociation (D_B) is less and as such the trough of the potential energy curve becomes shallower at higher electronic levels. At sufficiently high an electronic state, the potential energy curve takes the shape as at C, with no minimum. In such circumstances, there is no vibration rotation band with fine-structure and the molecules reaching that state must dissociate.

During an electronic excitation, certain conditions are obeyed as proposed in what is known as the *Franck-Condon Principle*. The principle states that during an electronic transition, the interatomic distance remains unaltered. This happens because electronic movement is much more rapid compared to nuclear movements. The period for electronic transition is of the order of 10^{-16} sec whereas the vibrational period is of the order of 10^{-13} sec. It is thus possible to represent the electronic transition by vertical lines (PP' , NN' , QQ' etc.) in potential energy diagrams (Fig. VII.18).

The Franck-Condon principle further states that an electronic transition would occur only when the atoms in the lower electronic state are in their extreme positions such as at P , L , Q , N etc. Only if the molecule is at zero vibrational level as is very often the case at room-temperature, the electronic transition may occur when the molecule is at its equilibrium distance as shown by ZZ' . Not only the extreme interatomic separation remains constant during transition but in the higher electronic state the same interatomic separation will be the amplitude of the new vibrational level. That is, this distance will be the shortest or longest atomic separation in the new vibrational level. The points P' , Q' , N' , Z' etc. shall be the extremities of their respective oscillations.

If during an electronic excitation, the molecule reaches a quantum level at Q' or above, the atoms from their shortest separation begin to expand to infinite distance because of high vibrational energy, thus leading to dissociation. It is clear from the diagram that an absorption of energy equal to $(\Delta E_{el} + D_B)$ by a molecule in state A will lead to dissociation. Similarly when a molecule takes up a photon as to be excited to the C-state, it will result into dissociation. For any electronic transition in which a molecule reaches a vibrational level up to nearly Q' in state B, there shall appear electronic spectra with definite vibrational levels after transition.

Pre-dissociation. Henry (1924) first observed that in the absorption spectrum of S_2 -vapour some portions of the fine structure are diffuse and blurred. For this gas, in the region of wavelength greater than $2799 \text{ \AA}$ sharp lines are noticed. Between 2799 and $2741 \text{ \AA}$ the fine structure is blurred as if a continuum is ensuing. But at still lower wavelength the fine structure is again quite sharp. Later on such diffuse regions were noticed in many other spectra such as those of CH_3CHO , CH_3Cl , NO_2 , SO_2 , NH_3 etc. Such a phenomenon is termed 'Pre-dissociation.' In fact, three electronic states are involved in it.

Suppose 'B' and 'C' are the potential energy curves of two excited states of the molecule whose ground state curve is 'A', Fig. VII.19. The two curves B and C cross one another at the point R. Now a transition along LN from state A to B will produce normal vibration band with its fine structure. But when a transition like PQ is considered, such that the level QQ' is in the vicinity of R, there is a new possibility. When the atoms recede from Q (in state B) the energy changes along $QNRQ'$. As the energy-value approaches R, a transition from state B to state C occurs, particularly when the kinetic energy of vibration is small. Direct transition from A to C is not permitted. The energy of the system is now sufficient to cause dissociation in state C, although not so in state B. Hence the vibration in B is quantised but for transition like PQ and at still upper levels, the molecule may dissociate through state C in lesser time (10^{-13} sec) than the period of rotation (10^{-10} sec). Very often such pre-dissociation is observed in polyatomic molecules. In such a case, the curve B represents the excited state of a particular bond and the energy imported is not sufficient for the dissociation of this bond. This energy may pass on to another bond somewhere else in the molecule (state C) which would be sufficiently stretched to undergo dissociation. For example in CH_3CHO ,

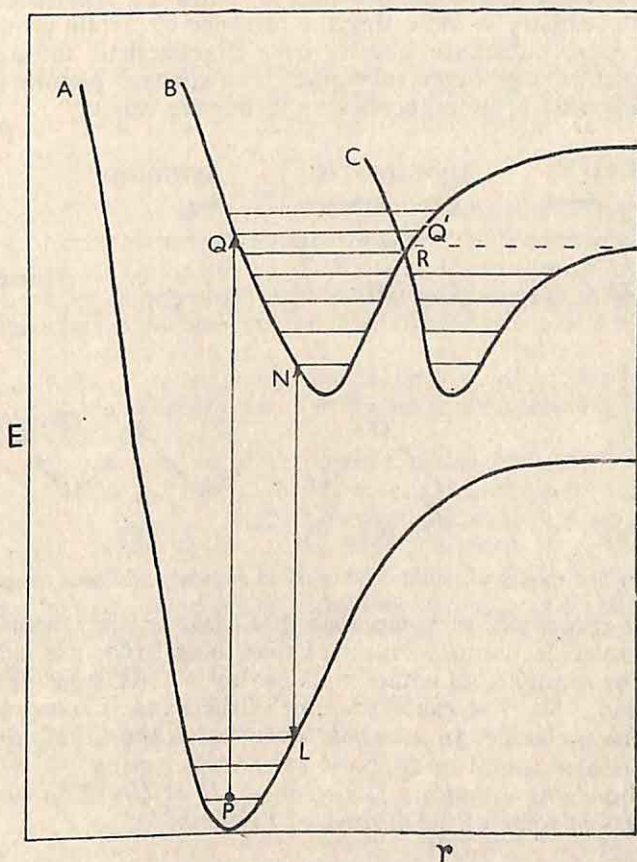


FIG. VII.19

the radiation is first absorbed to excite CO bond but subsequently dissociation occurs as $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3 + \text{CHO}$ (radicals). The spectrum reveals a region of pre-dissociation spectra.

VII.17. Infra-red Spectra and Chemical Constitution. Some of the direct applications of vibrational spectroscopy have been mentioned. The determination of force-constant, moment of inertia, the heat of dissociation of the bonds of a molecule can be deduced from a study of the infra-red spectra. There are also other very useful deductions.

The polyatomic molecules give rise to very complex vibrational spectra ; a complete and satisfactory interpretation of such spectra is often extremely difficult. A molecule with n atoms has $(3n-6)$ degrees of freedom. It will thus have $(3n-6)$ energy level patterns with individual spacings, and there will be as many bands. The number of vibrational bands becomes numerous when n is appreciably large and the spectra are quite complicated. If the vibrations are symmetrical with respect to a point or a plane, the interpretation becomes somewhat easier.

The molecule of water has three possible modes of vibration. Two of these are symmetric and the other asymmetric as shown in Fig. VII.20 below, for both linear and angular shapes of the molecule.

Since the mode (a) in linear structure is non-polar no vibration spectra for it is expected. So the linear shape of the molecule provides for only two possible modes of vibration, whereas the angular or bent shape of the molecule will exhibit three vibrational bands. For water, three bands with wave numbers of their three vibrational centres as $\bar{\nu} = 1595 \text{ cm}^{-1}$, 3652 cm^{-1} and 3756 cm^{-1} have been obtained ; the first two for the symmetric modes and the last for the asymmetric one. The bent shape of the molecule is thus confirmed.

Another invaluable assistance provided by infra-red spectroscopy is in the field of organic chemistry in indicating the presence of certain groups in a large molecule. Every pure substance has its own characteristic infra-red spectrum different from that of any other substance. The spectral picture thus helps in confirming and identifying an unknown sample of pure variety.

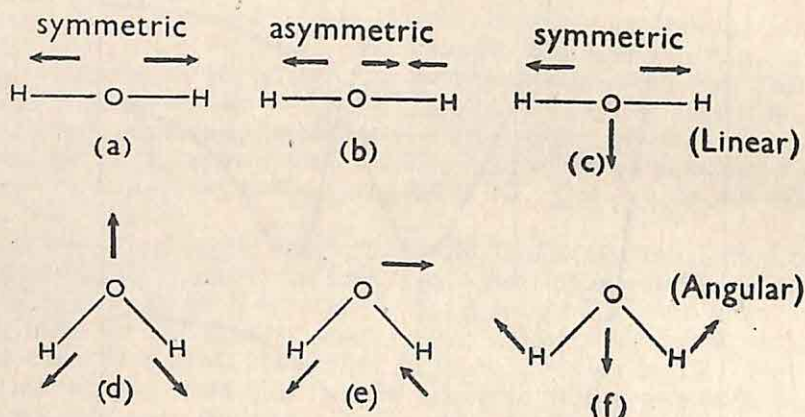


FIG. VII.20 The modes of vibration of H_2O in angular and linear structures.

The regular recurrence of some absorption bands when certain groups are present in the molecule points to the fact that these bands are characteristic of those groups. For example, all compounds having a 'C-H' bond exhibit bands in the region 3.2 and 3.5μ . The exact position of the band is somewhat influenced by the rest of the molecule. In aromatic compounds the C-H band is observed at 3.25μ which is also found in aliphatic substances having $-\text{C}=\text{CH}$ grouping. Similarly, N-H bonds have bands at 2.9 – 3.0μ , O-H at 2.7 – 2.8μ etc. The characteristic frequencies of some of the groups are tabulated below :

TABLE

Group	Band-frequencies, $\bar{\nu} \text{ cm}^{-1}$
$-\text{C}-\text{H}$	2880–3030
$=\text{C}-\text{H}$	3000–3120
$\equiv\text{C}-\text{H}$	3340
$\text{C}=\text{O}$	1660–1870
$\text{C}=\text{C}$	1600–1680
$-\text{C}\equiv\text{C}-$	2200–2260
$-\text{O}-\text{H}$	3500–3700
$-\text{N}-\text{H}$	3300–3500

These are most useful in confirming the presence of a group in a molecule. In a mixture, the positions and intensities of the bands for a particular substance are not affected by the presence of other components. So, in a mixture of closely related compounds, the identification as well as the quantitative estimation of a particular component can be spectroscopically ascertained, even if the chemical methods fail.

VII.18. Electronic Spectra. The electronic spectra are studied both in emission and in absorption. When an electron of a molecule is promoted from a low energy orbital (say ground state) to a higher energy state, radiations are absorbed in discrete amounts giving rise to absorption bands. On the other hand the return of an excited molecule to lower electronic states, energy released leads to emission spectra. Relatively large amounts of energy changes (about 10^2 Kcals per mole) are involved in these and the spectra are therefore found in the visible or ultraviolet region.

The electronic spectra are very complex in nature. For detailed treatment of such spectra, a text on molecular spectroscopy is to be consulted, only the basic principle is enunciated here. In spite of the complex nature of such spectra, the spectroscopists prefer the electronic spectra for they appear in visible-ultraviolet region where the handling of the experimental technique is much easier than in the infra-red. The other advantages offered by electronic spectra are that information about the excited state of the molecule and the heat of dissociation is easily obtained. Homopolar molecules which have no spectra in the infra-red or in microwave region also show electronic spectra.

Any change in the electronic state is associated with simultaneous changes in vibrational and rotational levels. We have seen in connection with the potential energy curves how the vibrational energies alter during a change in the electronic state of a molecule. When an electronic state is altered, there is usually a large number of changes in vibrational levels, each of which gives rise to a band. In each of these bands again there are innumerable lines due to rotational transitions. This makes the electronic spectra, even of very simple molecules, quite complicated.

Now, the energy of the molecule

$$E = E_{el} + E_{vib} + E_{rot}$$

In two electronic states, we can express them, as

$$E = E_{el} + (v + \frac{1}{2})h\omega - (v + \frac{1}{2})^2hx\omega + Bhj(j+1)$$

and

$$E' = E'_{el} + (v' + \frac{1}{2})h\omega' - (v' + \frac{1}{2})^2hx'\omega' + B'hj'(j'+1)$$

where v and v' are the vibrational quantum levels in two states with different fundamental frequencies ω and ω' ; the rotational constants B and B' consequently will be different as also anharmonic factors x and x' . Subtracting,

$$\Delta E = h\nu_e + (v + \frac{1}{2})h\omega - (v' + \frac{1}{2})h\omega' - \{(v + \frac{1}{2})^2hx\omega - (v' + \frac{1}{2})^2hx'\omega'\} + Bhj(j+1) - B'hj'(j'+1)$$

where $E_{el} - E'_{el} = h\nu_e$, i.e., the energy of the radiation absorbed or emitted had there been pure electronic energy-change.

On the other hand, the change in vibrational level ($\Delta v = v - v'$) may have any integral value,

$$\Delta v = 0, \pm 1, \pm 2, \pm 3, \pm 4 \dots \text{etc.},$$

whereas, the rotational transitions for any of these vibrational bands, $\Delta j = \pm 1$. The frequency of the radiation absorbed (or emitted) will then be given by,

$$\nu = \{ \nu_e + (v + \frac{1}{2})\omega - (v' + \frac{1}{2})\omega' - (v + \frac{1}{2})^2x\omega + (v' + \frac{1}{2})^2x'\omega' \} + Bj(j+1) - B'j'(j'+1) \dots \text{(VII.41)}$$

The terms within the parantheses on the right side, it is obvious, indicate the frequency of the centre of a band to which the fine structure is contributed by the rotational terms. Denoting the frequency of the centre of the band by ν_0 ,

$$\nu = \nu_0 + Bj(j+1) - B'j'(j'+1).$$

Now when $\Delta j = +1$, i.e., $j \rightarrow j+1$, we have the R-branch,

$$(a) \quad \nu_R = \nu_0 + Bj(j+1) - B'j(j-1) = \nu_0 + (B+B')j + (B-B')j^2$$

Again, when $\Delta j = -1$, i.e., $j-1 \rightarrow j$, we have the P-branch

$$(b) \quad \nu_P = \nu_0 + Bj(j-1) - B'j(j+1) = \nu_0 - (B+B')j + (B-B')j^2$$

Putting different integral values to j in (a) and (b) we can have the fine structure lines of the band. These lines evidently cannot be equispaced.

VII.19. Raman Spectra. When a beam of monochromatic light is passed through a transparent medium, a portion of light is scattered in all directions. The frequency of the scattered rays is the same as that of the incident beam. This is known as Rayleigh scattering. But a careful spectroscopic examination of the scattered rays reveals some faint lines other than those due to Rayleigh scattering. That is, a small portion of the rays are scattered with a different frequency. This was first observed by Raman in 1928 and the phenomenon is called *Raman scattering*.

In Rayleigh scattering the encounter between a photon and a molecule is an elastic one and hence the frequency of the scattered radiation remains unaltered. In Raman scattering since there is a change in frequency, and hence in energy, the collision between a quantum of radiation and a molecule is inelastic; the quantum either gives some energy to the molecule or takes it from the same.

An explanation of the Raman effect, based on quantum theory, may be made as follows: A molecule initially at level A with energy E_A absorbs the quantum of radiation $h\nu_i$ and is raised to the level X temporarily; ν_i is the frequency of the incident radiation. Then the energy at level X is $E_A + h\nu_i$. The molecule then emits a radiation of a different frequency (ν_s) and comes down to the level B . The energy of the molecule (E_B) now is $E_A + h\nu_i - h\nu_s$.

$$\begin{aligned} \text{i.e.,} \quad & E_A + h\nu_i - h\nu_s = E_B \\ \text{or} \quad & h\nu_i - h\nu_s = E_B - E_A \\ \text{or} \quad & h\Delta\nu = E_B - E_A \end{aligned}$$

That is, the energy which has been transferred to the molecule is $h\Delta\nu$. The change in frequency corresponding to this energy change is $\Delta\nu (= \nu_i - \nu_s)$. This frequency-change is called the *Raman frequency*.

Generally ν_s is less than ν_i , i.e., energy is taken up by the molecule ($E_B > E_A$). But it is also found that sometimes the molecule emits more energy than it was absorbed. The result is that $h\nu_s > h\nu_i$.

The Raman-scattered lines with lesser energy, i.e., those which are formed on the long wavelength side are called *stokes lines* and those which are formed on the short wavelength side of the incident beam are called *antistokes lines*.

The experimental results show that the Raman frequencies ($\Delta\nu$) are always of the order of 200 to 5000 cm^{-1} . That is the Raman frequencies belong to the infra-red region of the spectrum. In other words, the energy changes in the molecule during Raman scattering are those which would lead to infra-red spectra. It is thus rightly concluded that the energy difference between incident and scattered beam is used up in changing the vibrational energy level of the molecule. The lowest Raman frequency for a molecule should correspond to the equilibrium vibration frequency.

The energy-change in fundamental vibration band of the infra-red is given by (equation VII.31) $\nu = 0$ to $\nu = 1$, $\Delta E = h\omega - 2xh\omega = h\omega(1-2x)$.

Assuming this energy-change occurs in (lowest) Raman effect,

$$h\Delta\nu_R = h\omega(1-2x) \text{ or Raman frequency, } \Delta\nu_R = \omega(1-2x).$$

But $\omega(1-2x)$ is the centre of the fundamental vibration band where no spectral line is observed. Raman frequencies will thus be the centres of the vibration bands. This is corroborated from experimental findings. The observed Raman frequencies and the centres of vibration bands from infra-red spectra are compared below:

Molecules	Spectra	
	Infra-red, $[\omega(1-2x)]$	Raman ($\Delta\nu_R$)
HCl	2886 cm^{-1}	2886
NO	1879	1887
CO ₂	2144*	2145
N ₂	2331*	2335+
O ₂	1554*	1554+

* From electronic spectra with gases.

+ In liquid state.

These confirm that in Raman scattering vibrational changes are involved. Sometimes Raman lines with very small difference in frequency with the exciting radiation are obtained close to the line of the latter. The energy-changes are so small that these are considered to be due to pure rotational transitions. Raman effect may thus introduce vibrational and rotational changes in the molecule.

There are however some interesting characteristics in Raman scattering. The Raman frequency is independent of the frequency of the incident radiation and depends only on the medium. For this reason, any convenient source of radiation can be used. Although the frequency-shifts correspond to the infra-red region, these are very easily investigated and determined from the scattering in visible regions. The centres of vibrational bands which are forbidden in the infra-red spectra (since $\Delta j \neq 0$) are directly produced in the Raman spectra. Homopolar molecules cannot exhibit vibration-spectra but these respond to Raman scattering. In rotational Raman scattering, the quantum levels change by two instead of one, i.e., $\Delta j = \pm 2$. Since the fundamental frequency is available from Raman spectra, the evaluation of force-constant, moment of inertia etc. is also possible.

A wealth of information is available from the study of Raman spectra. The most important application of Raman effect is in the determination of the constitution of organic molecules. As in infra-red spectroscopy, definite Raman frequencies are associated with different linkages and these are the same as in vibrational spectra. The Raman frequencies for C—H linkage is about 2800 cm^{-1} and those for C $\equiv$ C about 2100 cm^{-1} , for C=C about 1600 cm^{-1} and so on. The results of examination of Raman scattering are thus helpful in establishing the constitution of an organic molecule.

Halides like NaCl, KCl, CaCl_2 etc. do not show any Raman frequency, but non-metallic chlorides and chlorides like HgCl_2 , Hg_2Cl_2 , ZnCl_2 etc. have intense Raman lines. This proves the existence of vibrational levels in Hg_2Cl_2 etc. confirming their covalent nature.

XO_4 type radicals such as SO_4^{--} , SeO_4^{--} etc. have definite Raman frequencies in the region $800\text{--}900\text{ cm}^{-1}$. But with telluric acid, the Raman frequency is about 648 cm^{-1} , far away from those of SO_4^{--} , etc. This shows that telluric acid cannot have TeO_4^{--} radical in it. Telluric acid is $\text{Te}(\text{OH})_6$ instead of H_2TeO_4 , $2\text{H}_2\text{O}$.

G. ABSORPTION OF LIGHT : SPECTROPHOTOMETRY

VII.20. Spectra of Liquids. The rotational, vibrational and electronic spectra which have been considered in the previous sections are produced with their fine structures when the substance is taken in the gaseous state. But in liquid state or in a state of solution, due to strong molecular interaction the fine structures in these spectra seldom appear. In the electronic transitions occurring in the visible and ultraviolet region, with liquids or solutions, the vibrational spacings are indistinguishable due to their overlapping. So in such spectra the vibrational bands along with their rotational fine structures disappear and instead are obtained continuous broad electronic bands. Although sharp structural features are not available, yet the absorption bands in the visible and ultraviolet regions have proved interesting study.

When the energy involved in electronic transitions is large the bands appear in the ultraviolet but with lesser energy-change the electronic absorption bands are formed in the visible region. It is only the coloured substances which would exhibit absorption band in the visible region. For, the colour of a substance determines the portion of white light it has not absorbed and has transmitted. The green colour of the NiCl_2 solution means that it has absorbed the red and transmitted the green out of the white light. The colourless alcohol or NaCl solution transmits the white light entirely and no visible radiation is absorbed. These may have absorbed some ultraviolet radiations. In our present study we are concerned with the radiations which are absorbed and the extent to which the absorption occurs.

The ultra-violet spectra are concerned with electronic transition from lower to higher orbitals. Usually the non-bonding (n -) lone pair of electrons are less strongly bound in a molecule. Of

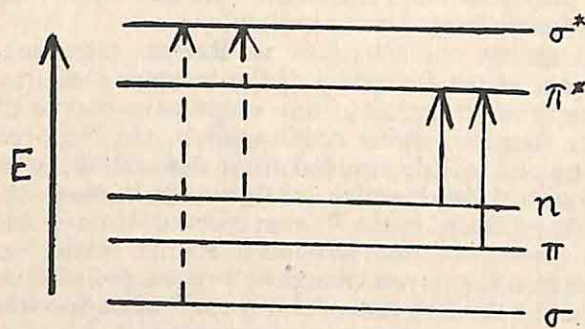
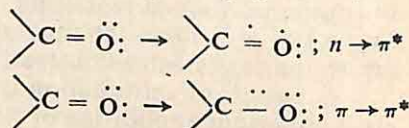


FIG. VII.21

the bonding electrons σ -electrons are at a lower energy level than the π -electrons. The absorption of radiant energy by organic molecules leads to transitions like (i) bonding π -electron to higher anti-bonding π^* -electron; (ii) non-bonding n -electrons to higher anti-bonding π^* -electrons; i.e., $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. Besides these, transitions of the type $\sigma \rightarrow \sigma^*$, and $n \rightarrow \sigma^*$ also occasionally occur. (Fig. VII.21).



When light is passed through a liquid or a solution, the absorption does not occur at all wavelengths. At a particular wavelength or within a small range of the same, the light is considerably absorbed. And in the shorter or longer wavelength side the absorption is very little. Hence if we plot the amounts of light absorbed (from an observation of the loss of intensity of emerging radiation) against wavelengths, we obtain a maximum at the absorption-range (Fig. VII.22). Every substance has got its specific absorption curve. The decrease in intensity of the radiation in its passage through the absorbing medium is governed by two Laws—Lambert's Law and Beer's Law.

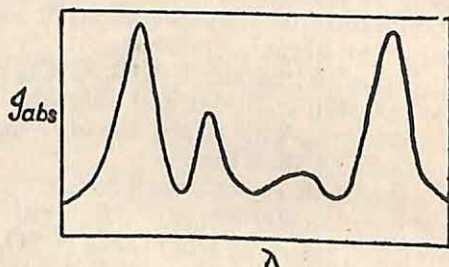


FIG. VII.22

Lambert's Law states that the rate of decrease of intensity with the thickness of absorbing medium is proportional to the intensity of the penetrating radiation. Consider a thin layer of the medium of thickness dl and let I be the intensity of the radiation entering it, then

$$\frac{dI}{dl} = -kI \quad \text{or} \quad \int_{I_0}^I \frac{dI}{I} = - \int_0^l k dl$$

$$\text{or} \quad \ln \frac{I}{I_0} = -kl$$

$$\text{i.e.,} \quad I = I_0 e^{-kl} \quad \dots \text{(VII.42)}$$

where I_0 is the intensity at $l = 0$, and I , the intensity at distance l . The constant k is called the 'absorption coefficient' of the substance. The equation may also be written as,

$$I = I_0 \cdot 10^{-al} \quad \dots \text{(VII.43)}$$

where $a = 0.4343 k$ and is termed 'extinction coefficient'. It is obvious that the proportion of the amount of light absorbed (I/I_0) with equal thickness (l) of the absorbing material will be the same and this proportion is independent of the intensity of the incident light.

If l denotes the thickness at which the intensity is decreased to one-tenth, then from equation (VII.43),

$$a = \frac{1}{l} \quad (l \text{ is expressed in centimetres})$$

When the absorbing substance is present in solution, the absorption of radiation will also depend upon the concentration of the solution, **Beer's Law** states that *the rate of decrease in intensity of radiation absorbed is proportional to the thickness of the medium and also to the concentration of the solute*. Hence, using same symbols,

$$\frac{dI}{dl} = k'l.c \quad (\text{where } c = \text{concentration})$$

$$\text{Integrating} \quad I = I_0 e^{-k'cl} \quad \dots (\text{VII.44})$$

$$\text{or} \quad k' = \frac{1}{cl} \ln \frac{I_0}{I} \quad \dots (\text{VII.44a})$$

where k' is called the '*molar absorption coefficient*'. It is evident that if the concentration is doubled and the thickness of the layer of solution be halved, the extent of absorption will be the same.

$$\text{Rewriting,} \quad I = I_0 10^{-\epsilon cl} \quad \dots (\text{VII.45})$$

so that ϵ , called '*molar extinction coefficient*' is given by $\epsilon = 0.4343 k'$. The value of ϵ is specific for a given substance at a given wavelength of the incident beam.

The quantity $\log \frac{I_0}{I}$ is called optical density or absorbancy (D) of the medium,

$$\text{so that} \quad D = \log \frac{I_0}{I} = \epsilon cd \quad \dots (\text{VII.46})$$

(d = thickness of the medium)

When a system contains several absorbing substances, each of these contribute independently to the space-rate of absorption of light, *i.e.*,

$$D = \epsilon_1 c_1 d + \epsilon_2 c_2 d + \epsilon_3 c_3 d + \dots = \sum \epsilon_i c_i d \quad \dots (\text{VII.47})$$

when concentration is expressed in moles/litre and d in centimetres.

Again, when $\log \frac{I_0}{I}$ is plotted against concentration of a solution taken in a column of definite thickness a straight line, as expected, is obtained. From the slope of the line the molar extinction coefficient is easily calculated.

To analyse a mixture having n components, D is measured at n wavelengths at which ϵ_1, ϵ_2 , etc. are known for each component, provided that ϵ_1, ϵ_2 , etc. are sufficiently separated.

An absorption curve nowadays can easily be obtained with the help of a photoelectric spectrophotometer. Beams of different monochromatic light obtained through special filters mounted on a dial are allowed to pass through a cell with pure solvent and also an identical cell with the solution. The transmitted light falls on to a photocell which directly registers the ratio I_0/I at each wavelength. It is thus an easy matter to find out the absorption peaks as also the value of molar extinction coefficient.

The study of the absorbances at, and the position of, the maxima provides us useful information for identification of typical functional groups in organic molecules. Molecules, in which double or triple bonds are present, have stable excited states to give rise to near U-V spectra. Hence, the occurrence of such a spectra helps us in detecting and identifying unsaturation. Saturated molecules of hydrocarbons, alcohols, ethers etc. are transparent in the near ultra-violet. Compounds having only one multiple bond, such as acetone, acetic acid etc. show absorbance of very low intensities and hence not quite suitable for identification. When two or more double (or triple) bonds exist separated by two or more single bonds, the absorbance practically become additive. On the other hand, if two multiple bonds be separated by one single bond, *i.e.*, in conjugated bonds, an unusually large absorbance results. Some of the experimental values U-V maxima and absorbances are given in the table.

TABLE

Group	Name	$\lambda_{max}(m\mu)$	ϵ	Group	Name	$\lambda_{max}(m\mu)$	ϵ
>C=O	acetone	279	15	>C=C-C=C<	butadiene	217	21000
>C=O	acetaldehyde	290	17	>C=C-C=O	crotonaldehyde	217	16000
-COOH	acetic acid	208	32	>C=C-COOH	crotonic acid	206	13500
-COOR	ethyl acetate	211	57	C ₆ H ₆	benzene	255	230

Example 1. On passing monochromatic light through a 0.04 molar solution in a cell 2 cms thick, the intensity of the transmitted light was reduced to 50%. Calculate the molar extinction coefficient.

Given $I/I_0 = 0.5$,

$$\text{So } \epsilon = -\frac{1}{c \cdot l} \cdot \log \frac{I}{I_0} = -\frac{1}{(0.04) \times 2} \log 0.5 = 3.76 \text{ litres mole}^{-1} \text{ cm}^{-1}$$

Example 2. A dye solution containing 1 gm per 100 c.c. transmitted 60% of the blue light in a cell 1 cm thick.

(a) What percentage of light would be absorbed by a solution containing 2 gm per 100 c.c. in the same cell?

(b) What should be cell thickness so that 90% of the light is absorbed by the original solution?

(i) Let c be the molar concentration of the original solution then the new solution has a concentration $2c$.

Hence, $\log (0.6) = -\epsilon \cdot c \cdot l$

and $\log (x) = -\epsilon \cdot 2c \cdot l$

where x is the proportion of light transmitted.

So $\frac{\log x}{\log (0.6)} = 2$, whence $x = 0.36$ or 36%

Therefore, light absorbed = 64%.

(ii) Here, the concentration of the soln is the same and let l cm be the thickness of cell required to transmit only 10% light.

Then $\log (0.6) = -\epsilon \times c \times 1$

$\log (0.1) = -\epsilon \times c \times l$

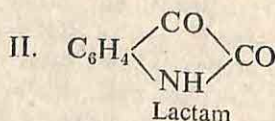
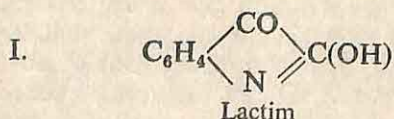
$\therefore l = \log (0.1) / \log (0.6) = 10.3 \text{ cms.}$

The absorption study often helps in quantitative estimation where chemical methods may fail. If in a mixture two components are present, whose individual optical densities are d_1 and d_2 , then the optical density of the mix is given by

$$D = [d_1 c_1 + d_2 c_2] l$$

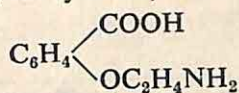
Carrying out measurements of optical densities at different wavelengths, we shall have two separate equations from which unknown concentrations c_1 and c_2 can be evaluated. The absorption or extinction coefficients are also used to find out the equilibrium constants in suitable cases.

But a very common use of spectrophotometry is in the structural problems especially of organic molecules. Compounds of similar structure give analogous absorption spectra (Hartley's rule). We may cite the historically famous example

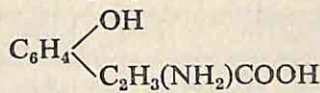


of isatin, which may have two possible structures. The absorption spectra of these two were compared with those of their methyl ether derivatives. It was found that N-methyl ether spectrum was similar to that of structure II above. Hence isatin was given the lactam structure.

Similarly, for tyrosine, two alternative structures proposed were



I. Derivative of oxybenzoic acid



II. A phenol

The absorption spectrum of tyrosine showed no resemblance to that of *p*-oxybenzoic acid but it did resemble that of phenol, thus confirming structure II for the amino-acid. Many other instances may be cited. The problems of keto-enol tautomerism have also been explained from the study of their absorption spectra.

H. MAGNETIC PROPERTIES

VII.21. Magnetic Properties of Substances. From the stand point of magnetic properties, substances have been broadly classified into three categories—diamagnetic, paramagnetic and ferro-magnetic. Diamagnetic substances are those which when placed in a magnetic field show a tendency to prevent the lines of force to pass through them whereas the paramagnetic substances prefer the lines of force to pass through them. This is schematically shown in Fig. VII.23.

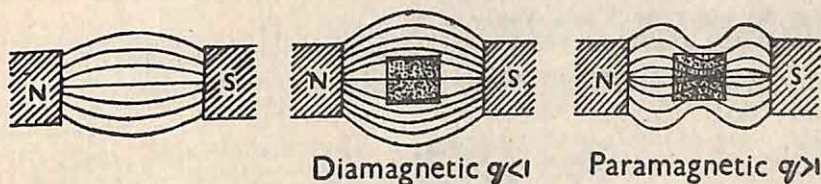


FIG. VII.23 Behaviour of diamagnetic and paramagnetic materials.

Ferromagnetic substances show a strong attraction for the lines of force. Ferromagnetism is found only in a few substances like Fe, Ni etc. and is of immense importance in technology and need not be considered here.

The force f between two magnetic poles of strength m_1 and m_2 at a distance r is

$$f = \frac{m_1 m_2}{q r^2} \quad \dots \text{(VII.48)}$$

where q is the magnetic permeability of the medium between the poles. In vacuum and in air q is approximately taken as unity. The permeability is a measure of the tendency of the lines of force to pass through the medium in comparison with vacuum. For diamagnetic substances q is less than unity and for paramagnetic substance q is greater than unity.

The intensity of magnetism induced by unit field is called the magnetic susceptibility of a substance. The magnetic susceptibility is related to permeability by the equation,

$$q = 1 + 4\pi\kappa \quad \dots \text{(VII.49)}$$

where κ is the volume susceptibility.

The susceptibility per gram called the specific susceptibility (χ) is κ/ρ , where ρ is the density of the medium. Then,

$$\begin{aligned} q &= 1 + 4\pi\rho\chi \\ \text{i.e.,} \quad \chi &= (q-1)/4\pi\rho \quad \dots \text{(VII.50)} \end{aligned}$$

In diamagnetic substances $q < 1$, hence χ is negative while in paramagnetic substances $q > 1$, i.e., χ is positive. The molar magnetic susceptibility (χ_M) is obtained by multiplying specific susceptibility by mol. wt ;

$$\chi_M = \chi.M \quad \dots \text{(VII.41)}$$

The χ_M is of the order of (10^{-6}) c.g.s. unit for diamagnetic substances, and 10^{-3} for paramagnetic and 10^2 for ferromagnetic ones.

The Gouy's balance is used for measuring the specific magnetic susceptibility. The material under examination is taken in a cylinder of known cross-section (A) and is suspended from one arm of a balance such that the lower half of the cylinder is at the centre of the poles of an electromagnet (Fig. VII.24). This is counter-poised by wts. placed on the pan in the other arm of the balance. On switching current to the electromagnet, the cylinder will go up if the substance is diamagnetic, or it will go down if the substance is paramagnetic. If mg be the additional wt. to be added (or subtracted) to restore equilibrium, then, it is shown,

$$mg = \frac{1}{2}AH^2(\rho\chi - \rho_0\chi_0)$$

where H is the applied field and χ_0 and ρ_0 are the sp. magnetic susceptibility and density of air. This relation may be used to find out χ . But the process may be simplified by comparing the

data with a substance of known χ' using same field and same cylinder, so that

$$\frac{mg}{m'g} = \frac{\rho\chi - \rho_0\chi_0}{\rho'\chi' - \rho_0\chi_0}$$

At room temperature, $\rho_0\chi_0 \approx 0.03 \times 10^{-6}$

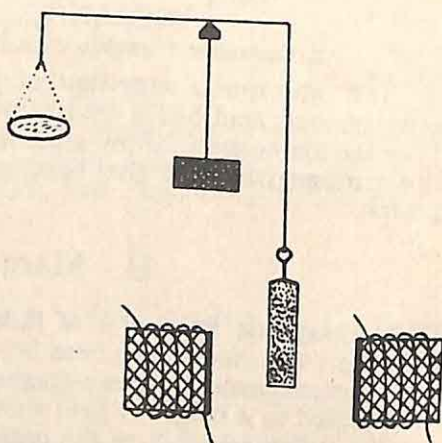


FIG. VII.24 Gouy's magnetic balance

VII.22. Diamagnetism. Every substance when placed in a magnetic field affects latter due to an induced magnetic moment. This is the diamagnetic effect which is similar to the 'distortion polarisation' of a molecule in an electric field. When the molecule concerned has a permanent magnetic moment then there would arise other additional effects. The diamagnetic effect arises from the orbital motion of the electrons around the nucleus. Application of a magnetic field causes an alteration in the orbital motion and a magnetic field is hence induced which opposes the applied field. The diamagnetic susceptibility is thus negative. The diamagnetic effect is independent of temperature and is practically the same for a substance in the gas or liquid phase. Langevin showed that for a monatomic molecule or any spherically symmetrical molecule, the diamagnetic susceptibility would be

$$\chi_M = \frac{-Ne^2}{6mc^2} \sum \bar{r}^2 \quad \dots (VII.52)$$

where $\bar{r}^2$ is the mean square of the orbital radii. This relation has been supported by experimental results.

The molar susceptibility in diamagnetic substances has been found to be an additive as well as a constitutive property, like molar refraction. Each atom and every structural configuration in a molecule make definite contribution to the molar susceptibility. From the determination of χ_M for a homologous series the contribution of a CH_2 -group, has been found to be $\chi_{\text{CH}_2} = 11.7 \times 10^{-6}$. The atomic susceptibilities were also separately determined. Some of the diamagnetic susceptibility constants and the values of χ_M for some substances are given here.

TABLE

Diamagnetic Susceptibility Constants		Molar Diamagnetic Susceptibility	
Atom or structure	Contributions	Substance	$\chi_M \times 10^6$
H	-2.93×10^{-6}	H ₂ O	-13
C	-6.00	CCl ₄	-66.6
N	-5.5	CO ₂	-21.0
Cl	-20.1	NH ₃	-18.0
Br	-30.6	N ₂ O	-19.0
I	-44.6	SO ₂	-18.0
O (alcohol)	-4.61	HCl	-25.0
O (ketonic)	+1.72	C ₂ H ₂	-12.5
C=C	+5.5	H ₂ S	-25.5
C=N	+8.15	C ₆ H ₅ COOH	-70.3
Benzene ring	-1.4	CH ₃ COOCH ₃	-43.1

Thus, the calculated χ_M for benzene would be for $6C = 6 \times (-6.00)$, for $6H = 6 \times (-2.93)$ and for the benzene ring (including the double bonds) $= -1.4$; the total is -54.99×10^{-6} whereas the experimental value is -55×10^{-6} .

VII.23. Paramagnetism. The molecules (or atoms or ions) of a paramagnetic substance possess a permanent magnetic moment, μ_m . This is due to the presence of one or more unpaired electrons in the molecule. These molecules then behave as tiny magnets. When an external magnetic field is applied, these tiny magnets tend to orient themselves parallel to the field similar to the polar molecules in an electrical field. But the orientation is opposed by the thermal motion of the molecules. In other words, the extent of orientation depends on temperature.

In fact the external magnetic field has both a diamagnetic induction effect (a_M) as also an orientation effect Z_M on the paramagnetic molecules. The molar susceptibility therefore would be

$$\chi_M = a_M + Z_M$$

Langevin (1905) derived from statistical considerations an expression for orientation magnetic effect and showed that Z_M is inversely proportional to temperature, i.e.,

$$Z_M = C_M/T, \text{ when the const. } C_M = \frac{\mu_m^2 \cdot N_0}{3k}$$

Hence

$$\chi_M = a_M + \frac{\mu_m^2 N_0}{3kT} \quad \dots \text{ (VII.53)}$$

Excepting in a few cases, a_M is very small compared to the other effect and is either ignored or evaluated from atomic susceptibilities. The determination of χ_M at one or more temperatures would enable us to find out the value of μ_m .

The magnetic moment μ_m is expressed in units of ergs gauss⁻¹. But very often more convenient units are those of Bohr magnetons, μ_B , which is evaluated in the following way.

Consider the single electron of the hydrogen atom moving with velocity, v in its lowest orbit with a radius r . Then the current produced would be

$$i = \frac{v \cdot e}{2\pi r}, \quad (e = \text{charge of the electron})$$

When a current is passing in a coil a magnetic field is produced perpendicular to the coil. This field is equal to that of a magnet with moment μ_m , such that

$\mu_m = \frac{i \cdot A}{c}$, [where c = velocity of light and A = area of the coil). Hence the

moment μ_m in the lowest orbit of the hydrogen atom would be

$$\mu_m = \frac{v \cdot e}{2\pi r} \cdot \frac{\pi r^2}{c} = \frac{v e r}{2c}$$

$$\text{or } \mu_m = \frac{mvr \cdot e}{2mc} = \frac{e}{2mc} \cdot \frac{h}{2\pi} \quad \left(\text{since Bohr's } mvr = \frac{h}{2\pi} \right)$$

$$\text{or } \mu_m = \frac{eh}{4\pi mc} = 9.27 \times 10^{-21} \text{ ergs gauss}^{-1} \quad \dots \text{ (VII.54)}$$

(substituting standard values)

This quantity of moment has been defined as the *Bohr magneton*, μ_B . The observed moment has to be divided by this in order to express the same in Bohr magnetons.

Both the orbital motion of the electron as also the spinning of the electron about its own axis should contribute to the magnetic moment of the molecule or atom or ion. But in a polyatomic system the orbital motions are so rigidly oriented in respect of the nuclei that the applied field cannot effect the same in any way. Even for monatomic species in liquid or solid states (where such studies are usually made), the influence of the solvent molecules or their mutual cohesion prevent any alteration of the orbital motion due to an external field. So in most cases (excepting the rare-earth ions), the orbital magnetic moment is inoperative; we are to consider only the contribution from the spinning of the electron. It has been shown from quantum mechanical treatment that

$$\mu_m = 2\mu_B \sqrt{S(S+1)} \quad \dots \text{ (VII.55)}$$

where S is the spin quantum number, having values $\frac{1}{2}, 1, \frac{3}{2}, 2, \dots$ etc. Each unpaired electron contributes $\frac{1}{2}$ towards the value of S . Thus, we have some definite values of μ_m for molecules with one, two, three $\dots$ unpaired electrons, as in the table below.

TABLE

No. of unpaired electrons	Spin quantum number S	μ_m in Bohr magnetons	$\chi_m = \frac{\mu_B^2 N_0}{3kT} \cdot 4S(S+1)$
1	$\frac{1}{2}$	1.73	1260×10^{-6}
2	1	2.83	3360
3	$\frac{3}{2}$	3.88	6290
4	2	4.90	10100
5	$\frac{5}{2}$	5.91	14700

$$\left[\text{Since } \chi_m = \frac{N_0}{3kT} \mu_m^2 = \frac{N_0}{3kT} \left((2\sqrt{S(S+1)})\mu_B \right)^2 = \frac{4N_0\mu_B^2}{3kT} S(S+1) \right]$$

Evidently, determination of molar magnetic susceptibility will lead to the knowledge of the number of unpaired electrons present in the molecule or the ion concerned. Thus, at ordinary temperature the molar susceptibility of oxygen was found to be 3360×10^{-6} i.e., a moment of about 2.8 Bohr magnetons. Oxygen molecule has therefore two unpaired electrons and the bonding shall be



The existence of an unpaired electron in molecules of NO, ClO₂ etc. suggested from other evidences has been confirmed from the susceptibility measurement of 1300×10^{-6} e.m. units in these cases.

The molecule of mercurous chloride does not show any paramagnetic susceptibility, and is purely diamagnetic. This indicates that the molecule should be Hg₂Cl₂ and not HgCl, as the latter would have made it paramagnetic. Similarly, hypophosphoric acid, if regarded as H₂PO₄, would be paramagnetic as it would contain an odd electron. Its pure diamagnetic character proves it to be H₄P₂O₆. These are just a few of the innumerable examples which illustrate the usefulness of paramagnetic studies in the elucidation of structures. In the cases of ions, specially complex ions and in radicals also, paramagnetic study reveals the number of unpaired electrons in them and hence the structure. In the ferrocyanide ion, Fe(CN)₆⁴⁻, the configuration is [Ar]3d¹⁰4s²4p⁶

the 3d-level is completed and the ion is diamagnetic, whereas in ferricyanide ion $\text{Fe}(\text{CN})_6^{3-}$, the configuration $[\text{Ar}]3d^5 4s^2 4p^6$ the presence of an odd electron in 3d-level should make it paramagnetic. These are substantiated from experimental observations.

I. NUCLEAR MAGNETIC RESONANCE

VII.24. Nuclear Magnetic Resonance (NMR). The protons and neutrons present in nuclei of atoms spin on their own axes and each of them possesses angular momentum $\frac{1}{2} (h/2\pi)$. The net resultant of the angular momenta of all the nuclear particles, called the *nuclear spin*, is given by $\sqrt{I(I+1)} \frac{h}{2\pi}$, where I is the spin

quantum number. The nuclear spin depends upon the number of particles in the nucleus. There are three broad principles for the nuclear spin : (i) A nucleus with an odd mass number has a half integral spin, (ii) a nucleus with an odd number of protons and an odd number of neutrons has an integral nuclear spin, (iii) a nucleus with an even number of protons and an even number of neutrons has zero nuclear spin. Thus, ^1H , ^{11}B , ^{13}C , etc. have magnetic moments having spin of $\frac{1}{2}$; whereas ^{12}C , ^{16}O , etc. have no magnetic moment.

The nucleus considered as a charged spinning body possesses a magnetic moment μ_N . Nuclear magnetic moments are very small and are measured in units of nuclear magnetons (n.m.). As in the case of Bohr magneton in atoms, the nuclear magneton 1 n.m. = $eh/4\pi m_p c$ where m_p is the mass of the proton. Substituting standard values, 1 n.m. = 5.0493×10^{-24} ergs gauss $^{-1}$ i.e., 1 n.m. is less than one-thousandth of a Bohr magneton. For hydrogen nucleus, the magnetic moment is $\mu_N = 2.7927$ n.m.

When a nucleus is placed in a homogeneous external magnetic field of strength H , it will behave as a magnet and tend to orient itself in relation to the field. In such circumstances, its potential energy is given by $\epsilon = -\mu_N H \cos \theta$, where θ is the angle between its magnetic axis and the direction of the field. This energy is quantised and can have some definite values only.

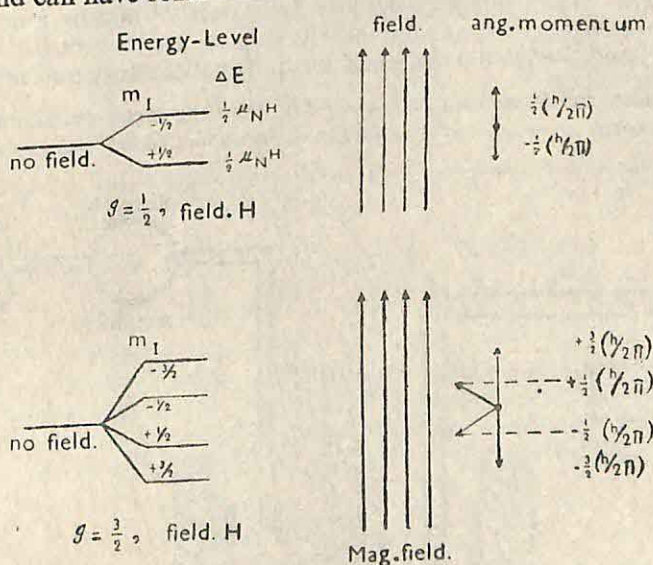


FIG. VII.25 The allowed energy levels and angular momenta of nuclei with $I = \frac{1}{2}$ and $I = \frac{3}{2}$.

The components of the angular momentum of the spinning nucleus in the direction of the field are given by $m_I \frac{h}{2\pi}$, where m_I can have the allowed values of $-I, -I+1, -I+2, \dots, 0, \dots, I-1, I$; i.e. a total of $(2I+1)$ possible values.

In other words, the nucleus may have $(2I+1)$ possible orientations with respect to the field. In Fig. VII.25 are shown the possible orientations of angular momentum vector and energy levels, for nuclei with $I = \frac{1}{2}$ and $I = \frac{3}{2}$.

The energies of the allowable states may be represented by

$$E = -\mu_N H \cdot \frac{m_I}{I}$$

Hence, the difference in energy between two levels would be

$$\begin{aligned} \Delta E &= -\frac{\mu_N H}{I} [m - m'] \\ &= -\frac{\mu_N H}{I}, \quad (\text{when } \Delta m_I = 1) \quad \dots \quad (\text{VII.56}) \end{aligned}$$

Thus, for the nucleus of ^1H with spin $\frac{1}{2}$, we have two states

- (a) state of higher energy, $\epsilon = +\mu_N H$, (since $m_I = -\frac{1}{2}$, $\theta = 180^\circ$)
 - (b) state of lower energy, $\epsilon = -\mu_N H$, (since $m_I = +\frac{1}{2}$, $\theta = 0^\circ$)
- i.e., $\Delta\epsilon = 2\mu_N H$.

Now if ν be the frequency of a radiation which would be in resonance with the energy-level spacings given in equation (VII.56), we have

$$h\nu = \frac{\mu_N H}{I}, \text{ i.e., } \nu = \frac{\mu_N H}{hI} \quad \dots \quad (\text{VII.57})$$

The magnetic fields used for NMR studies is of the order of 10,000 gauss. With such a field, the frequency obtained for the radiation corresponding to nuclear magnetic energy-level spacing from eqn. VII.57 is about 50×10^6 cycles/sec, i.e., the frequency will be in the region of radio-waves. It is thus easily seen that if we use radio frequency waves on a nucleus placed in an external magnetic field, it might absorb a suitable frequency, satisfying eqn. VII.57, and will jump from lower to higher energy state orientating from a direction with the field to one against the field. When this happens, we are indeed obtaining a nuclear magnetic resonance or NMR. Most of the NMR studies are concerned with hydrogen nucleus ($I=\frac{1}{2}$) and the results obtained are quite satisfactory and revealing.

In 1946, Block and Purcell independently developed the experimental technique for study in NMR spectroscopy. A schematic presentation of the apparatus required is given in Fig. VII.26.

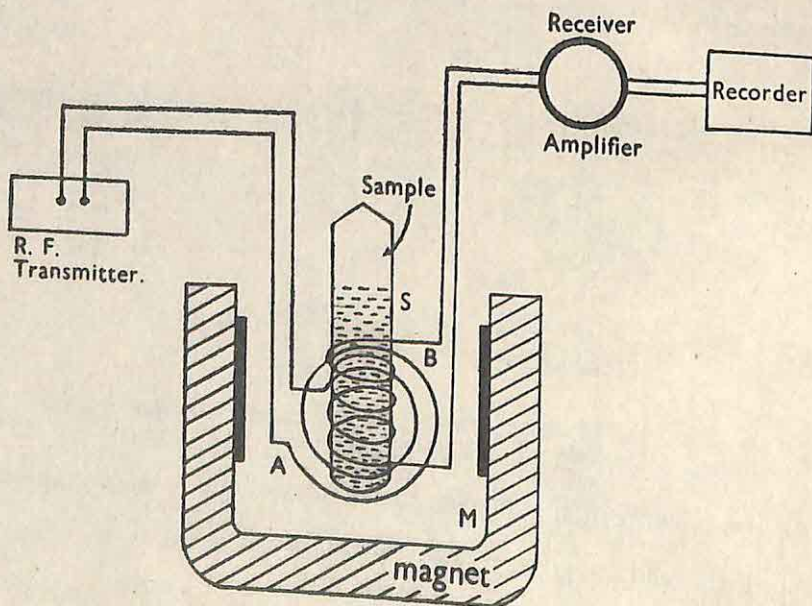


FIG. VII.26 NMR Spectrometer (schematic)

The sample, usually a liquid or a solid, is taken in a tube S placed between the poles of a huge magnet (M) of adjustable field H . A coil (A) surrounding the sample emits a definite pre-adjusted radio-frequency (40-60 magacycles) from a transmitter, while another coil (B) picks up any radiation emitted. The latter is carried to a receiver and amplified and finally to a cathode-ray oscillograph or recorder. The field strength H is gradually increased and the radiation will be absorbed only when the eqn. VII.57 is satisfied for a given ν , *i.e.*, when the nuclear energy-level spacing matches the quanta of radiation of given ν . When this condition is reached, there is resonance between the two and absorption occurs. On further increase of the field-strength, there is no absorption until again a correspondence is reached. These absorptions are detected directly from the oscilloscope or recorder, as shown in Fig. VII.27, (a) for low and (b) for high resolution, for $\text{CH}_3\text{CH}_2\text{OH}$.

To illustrate the application of the NMR spectra, the simple case of the resonance spectrum of ethyl alcohol may be taken. In this molecule, the nuclei of carbon and oxygen atoms have zero nuclear spin and will not produce any nuclear magnetic spectra. The NMR spectroscopy is thus concerned here with the protons in the hydrogen nuclei present having $I = \frac{1}{2}$. Since such a proton (^1H) has only two nuclear magnetic energy levels *i.e.*, one energy-level spacing, we should expect only one absorption peak in the resonance spectrum. But even at low resolution (Fig. VII.27) as many as three absorption peaks are actually obtained. This is due to the fact that the different hydrogen nuclei exist in the molecule in different

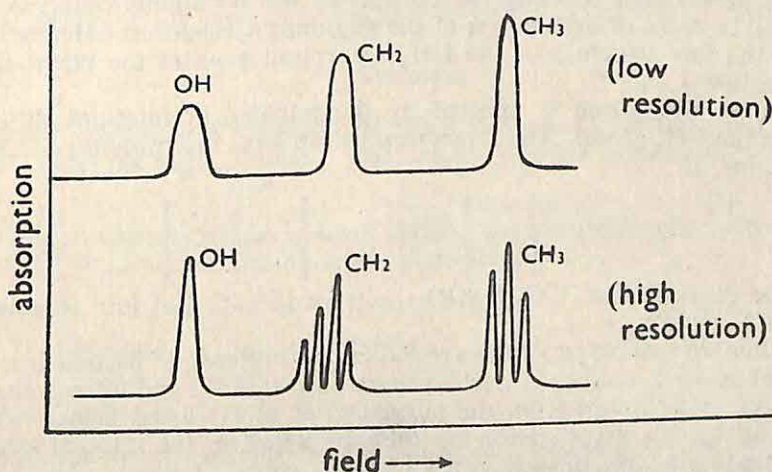


FIG. VII.27 NMR Spectrum for $\text{CH}_3\text{CH}_2\text{OH}$

environments. The electrical atmosphere and surroundings of the ^1H -nuclei in CH_3 -group are not the same as those for ^1H -nuclei in CH_2 -group or in OH -group. The different nuclei are differently shielded by the orbital electrons and the shielding is also affected by the nature of chemical bonding. The result is that the actual field H_A experienced by a nucleus is not the same as the applied field H , and these two are related as

$$H_A = H/(1 - \delta)$$

where δ , called *chemical shift*, depends on the electron distribution around the nucleus *i.e.*, on the chemical environment.

It is thus obvious that the absorption in the NMR spectrum for H-nucleus would appear at a frequency which depends on the chemical environment. A proton in the CH_3 -group and another in the OH -group of the alcohol have different environment and the actual field experienced by the two are different and hence absorption peaks will be different. Consequently, when the chemical environment is the same, *i.e.*, the nuclei occur in same groups or radicals, the absorption peaks

should be identical. For this reason, the chemical shift (δ) produced in the position of the spectral lines is usually expressed with reference to that of a standard substance.

$$\delta = \frac{H_{\text{sample}} - H_{\text{ref}}}{H_{\text{ref}}} \times 10^6$$

which is the difference in the magnetic field necessary for absorption compared to that necessary for some standard substance, say water. These absorption peaks can be used to identify functional groups containing the nuclei. The intensities of the three peaks in ethanol NMR-spectrum are in the ratio, 1 : 2 : 3, evidently corresponding to OH, CH₂ and CH₃ groups in which proton numbers are in that ratio.

When the resolution is high, the peaks give rise to fine structure. In this case, the peak for CH₂-group produces four closely packed absorption lines, and CH₃-group three. This is due to the interaction between the neighbouring nuclei. The CH₃-group is adjacent to the CH₂-group. Each proton in the CH₂-group has two possible orientations and when coupled these would produce three possible combinations :

$$\begin{array}{ccc} +\frac{1}{2} & +\frac{1}{2} & \\ \text{(both spins parallel)} & \begin{array}{cc} +\frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & +\frac{1}{2} \end{array} & \begin{array}{cc} -\frac{1}{2} & -\frac{1}{2} \end{array} \\ & \text{(opposed spins)} & \text{(both spins antiparallel)} \end{array}$$

Hence the actual field affecting the CH₃-group will be slightly different with the three possible states of orientation of the adjoining CH₂-group. Hence there is a triplet in the fine structure of the CH₃-absorption peak in the NMR-spectrum, with intensities 1 : 2 : 1.

Similarly CH₂-group is affected by the possible orientations of the three protons in the CH₃-group. The three protons can have four possible combinations of their spins, as.

$$\begin{array}{ccccccc} +\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} & & +\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ & +\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \\ & -\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} \end{array}$$

It is hence expected that CH₂(NMR) spectrum should split into four lines with intensities 1 : 3 : 3 : 1.

We thus see that NMR-studies reveal (a) the presence of particular functional groups (b) relative number of nuclei present in the group and (c) also the relative positions of these groups from the multiplicities of the lines. Hence NMR provides means for the investigation of intimate details of the internal structure of molecules not available through other methods.

VII.25. Electron Spin Resonance (ESR). Electrons possess spin and the values of the spin angular momentum are $\pm \frac{1}{2} h/2\pi$. These spinning charged particles have therefore a magnetic moment. In most molecules there are usually a large number of electrons occupying different orbitals. When all the occupied orbitals have paired electrons, the net electron spin is zero and the question of splitting of energy levels does not arise. But when a molecule or an ion has an unpaired electron as in free radicals or in atoms like those of lanthanides, the net spin is not zero. When such an ion or molecule is placed in a magnetic field, there is an interaction between the magnetic moment of the electron and the applied field. As in the case of the spinning nucleus, the electronic spin angular momentum is also quantised in the direction of the magnetic field. The result is that in the presence of the applied field, the energy is split up into different levels having values $+\mu_e H$ and $-\mu_e H$ where μ_e is the magnetic moment of the spinning electron. The spacing between the two energy levels is larger than that in the case of nuclear energy levels. When a field of 3000 gauss is applied, the frequencies corresponding to the energy-level spacing are found to be in the microwave region. An electronic spin resonance spectrum can thus be obtained in this region. Detailed only mention that the results of such ESR study help in establishing the presence and the number of unpaired electrons in a radical or an atom. The hyperfine structure or multiplicity of line, obtained in ESR spectrum due to interaction of the spin of the odd electron with magnetic nuclei of the molecule also reveals the structure and electron distribution in organic molecules.

References for further reading

- (1) *The Parachor and valency* : SUGDEN.
- (2) *Parachor and structure* : *Chem. Rev.* 53, 439, 1953 : QUAYLE.
- (3) *Optical rotatory power* : LOWRY.
- (4) *Polar molecules* : DEBYE.
- (5) *Dipole moments* : DEBYE.
- (6) *The structure of molecules* : SYRKIN AND DYATKINA.
- (7) *Dipole moments* : LE FEVRE.
- (8) *Dielectric behaviour and structure* : SMYTH.
- (9) *Nature of chemical bond* : PAULING.
- (10) *Molecular spectra and molecular structure* : HERZBERG.
- (11) *Spectra of diatomic molecules* : HERZBERG.
- (12) *Introduction to molecular spectroscopy* : BARROW.
- (13) *Infra-red and Raman spectra* : SUTHERLAND.
- (14) *Introduction to infra-red and Raman spectroscopy* : COLTHUP, DALY AND WIBERLY.
- (15) *Chemical application of infra-red spectroscopy* : RAO.
- (16) *Magnetochemistry* : BHATNAGAR AND MATHUR.
- (17) *Magnetochemistry* : SELWOOD.
- (18) *Nuclear Magnetic Resonance* : ANDREW.
- (19) *High resolution nuclear magnetic resonance* : POPLE, SCHNEIDER AND BERNSTEIN.
- (20) *Nuclear Magnetic resonance spectroscopy* : *J. Chem. Edn.* 1961, 38, 581 : ROBERTS.

Problems

1. At 12°C, the density of aniline is 1.028. What will be its surface tension? Use parachor equivalents from the Table. Compare your estimate with the experimental value of 44.7 dynes/cm. [Ans : 46.8]

2. Suggest possible structures for quinone, $C_6H_4O_2$. The observed parachor value for quinone is 236.8. Which of the proposed structures would you accept?

3. Given

substance	density	ref : index
acetone	0.7928	1.3620
acetic acid	1.046	1.3715

Calculate the molar refractions of the two compounds and compare with those obtained from the additivity rule. [Ans : (a) obs. 16.15, calc. 16.065 ; (b) obs. 13.303, calc. 12.972]

4. A primary alcohol, $C_{10}H_{18}O$ has the density and refractive index as $n_D = 1.4745$ and $d = 0.8893$, find out if there are double bonds in the molecule and if so, how many? [Ans : Two]

5. The dielectric constant and refractive index of a liquid ($M = 112$) at 25°C are 4.288 and 1.348 respectively. The density of the liquid is 1.108 gm/c.c. Calculate the values for its molar polarisation and molar refraction. [Ans : 52.85 ; 21.6]

6. What will be the refractive index of an ideal mixture of benzene and toluene containing 50% of each constituent by weight. The densities of benzene and toluene are 0.8790 and 0.8669 gm/c.c. respectively [use table of refraction equivalents].

7. Given, for a liquid at 20°C,

molar polarisation	$P_\infty = 58.5$ c.c.
refractive index	$n = 1.350$
density	$= 0.7136$ gm/c.c.

what is the dipole moment of the substance?

[Ans : = 1.315]

8. The dipole moment of chlorobenzene is 1.55d. The bond distance C_6H_5-Cl is 2.8 Å. Estimate the ionic character of the bond. [Ans : 11%]

9. 6.15 gm of an organic substance (*A*) was dissolved in 100 c.c. of alcohol. A portion of this solution in a 5-cm polarimeter tube gave a rotation of -1.2° . What is the specific rotation of *A*? What will be the rotation if this solution is diluted to twice its volume and the rotation is observed in a 50-cm tube?

[Ans : (a) -39° , (b) -6° .]

10. The microwave spectra of CO molecule gave $2h^2/8\pi^2I = 7.6 \times 10^{-16}$ ergs. Calculate the bond-length.

[Ans : $1.13 \text{ \AA}$]

11. The moment of inertia of a NO molecule is 16.5×10^{-40} gm-cm². What will be the energy at the first rotational level ($j = 1$)?

[Ans : $E_{rot} = 6.7 \times 10^{-16}$ ergs]

12. When light ($\lambda = 4200 \text{ \AA}$) was passed through a vapour of 10 cm layer, 80% was absorbed. Calculate the absorption and extinction coefficient.

[Ans : $9.69 \times 10^{-3} \text{ cm}^{-1}$; $22.32 \times 10^{-3} \text{ cm}^{-1}$]

13. Two isomeric compounds *A* and *B* of formula C_5H_{12} are both reduced to *n*-pentane on hydrogenation. *U-V* spectra showed : λ_{max} for *A* = $176 m\mu$, λ_{max} for *B* = $211 m\mu$. *I*-pentane has $\lambda_{max} = 178 m\mu$. What would you infer from these? Can you suggest structures for the two isomers?

14. How many NMR signals do you expect in the following :

(a) dimethyl ether (b) diethyl ether (c) acetone (d) benzene (e) toluene (f) ethyl benzene.

CHEMICAL STATISTICS

We have seen in chapter IV that in classical thermodynamics, the properties of a macroscopic system are defined in terms of variables upon which it depends. The temperature, pressure, energy etc. are taken as functions of state. In the development of thermodynamic relations, it is not necessary to take into account the constitution of the material system, *i.e.*, atomic theory is ignored. Thermodynamics does not concern itself about the nature, structure or the energy-states of the microscopic constituents of the system nor does it explain as to how the observed macroscopic properties of the system arise out of the properties of the microscopic parts.

A new approach, namely, that of statistical thermodynamics has since been made to calculate the macroscopic properties from suitable summation of the microscopic properties. In this procedure, the matter is pictured as composed of innumerable particles in motion. This motion of the particles is governed by the laws of dynamics and, in fact, subject to quantum mechanical principles. Even in the smallest system taken the number of particles is so large that it is impossible to follow the behaviour of every individual particle. Statistical methods are utilised to find out the properties of the system, particularly to ascertain what fraction of the molecules has a given energy. It is possible to establish that the thermodynamic laws are the necessary consequence of the quantum principles when statistical postulates are used. In this chapter attempt is being made to indicate the elementary principles involved in the statistical applications.

VIII.1. Thermodynamic Probability. Let us take a system of volume V containing n identical and distinguishable particles; n of course is very large. Let E be the total energy of the system whose temperature is T . All the particles will not have the same energy. Suppose n_0 particles are in energy-level ϵ_0 , n_1 particles are in energy-level ϵ_1 , n_2 particles in energy-level ϵ_2 , and so on.

The total energy of the system,

$$E = n_0\epsilon_0 + n_1\epsilon_1 + n_2\epsilon_2 + \dots n_i\epsilon_i + \dots = \sum n_i\epsilon_i$$

We also know,

$$n = n_0 + n_1 + n_2 + \dots n_i + \dots = \sum n_i$$

As the occupation numbers, $n_1, n_2, n_3 \dots$ etc. in different energy-levels change, the distribution also changes. There are obviously various ways of distribution. What will be the total number of possible distributions? This is similar to the arrangement of n boys in p -classes, so that one class has n_0 boys, another n_1 boys, and so on. This number is given by

$$P = \frac{n!}{n_0! n_1! n_2! \dots n_p!} = \frac{n!}{\prod n_i!}$$

The number of possible distribution of the n molecules in different energy-levels is

$$P = \frac{n!}{\prod n_i!} \quad \dots (A)$$

' P ' thus indicates the total number of possible complexions or microstates for a given combination and it has been called the "*thermodynamic probability*"*

$$\begin{aligned} \ln P &= \ln n! - [\ln n_0! + \ln n_1! + \ln n_2! + \dots \ln n_i! \dots] \\ &= \ln n! - \sum \ln n_i! \end{aligned}$$

* The thermodynamic probability P is proportional to the mathematical probability $W \left(= \frac{n!}{\prod n_i!} \times C^{-n} \right)$ where C^n is the total number of possible cases.

Since n , as also n_i are very large, we can apply Stirling's theorem,

$$\ln x! = x \ln x - x$$

We can then write,

$$\ln P = n \ln n - n - [n_1 \ln n_1 - n_1 + n_2 \ln n_2 - n_2 \dots]$$

$$\begin{aligned} \text{Or } \ln P &= n \ln n - \sum n_i \ln n_i - n + \sum n_i \\ &= n \ln n - \sum n_i \ln n_i \quad (\text{since } n = \sum n_i) \end{aligned} \quad \dots (B)$$

VIII.2. The Most-Probable Distribution (Boltzmann). We can now attempt to find out the most probable distribution. This will be achieved when the system attains equilibrium. When equilibrium is attained, *i.e.*, at equilibrium distribution the thermodynamic probability will be maximum. That is, at equilibrium, the magnitude of P , and therefore of $\ln P$, will be maximum. Hence at eqm., $d \ln P = 0$.

From equation (B) at equilibrium ;

$$d \ln P = d(n \ln n) - d(\sum n_i \ln n_i) = 0.$$

$$\text{i.e. } d(\sum n_i \ln n_i) = 0$$

$$\text{or } \sum \ln n_i dn_i + \sum dn_i = 0$$

$$\text{Since } \sum n_i = n = \text{constant}, \sum dn_i = 0,$$

$$\therefore \sum \ln n_i dn_i = 0 \quad \dots (C)$$

We must remember that for the given system the total energy E and the total number of particles n remain constant, *i.e.*,

$$n = \sum n_i ; \quad \text{or } dn = \sum dn_i = 0 \quad \dots (D)$$

$$E = \sum n_i \epsilon_i \quad \text{or } dE = \sum \epsilon_i dn_i = 0 \quad \dots (E)$$

Multiplying equations (D) and (E) by undetermined arbitrary multipliers α and β respectively and adding equation (C), we have

$$\sum \ln n_i dn_i + \alpha \sum dn_i + \beta \sum \epsilon_i dn_i = 0$$

$$\text{or } [\sum \ln n_i + \alpha + \beta \sum \epsilon_i] dn_i = 0.$$

Since α and β are independent, the restraining conditions are removed, and $dn_i \neq 0$, this relation will be true for any energy-level or cell ; hence

$$\ln n_i + \alpha + \beta \epsilon_i = 0$$

$$\text{or } n_i = e^{-\alpha} e^{-\beta \epsilon_i} \quad \dots (VIII.1)$$

This is the expression for the number of particles in each energy-level, α, β being unknown arbitrary constants.

$$n = \sum n_i = e^{-\alpha} \sum e^{-\beta \epsilon_i} \quad \dots (VIII.2)$$

$$\text{or } n_i = \frac{n \cdot e^{-\beta \epsilon_i}}{\sum e^{-\beta \epsilon_i}} \quad \dots (VIII.3)$$

This is known as the Boltzmann Distribution Law. It gives at a temperature T the fraction of total number of molecules which at eqm. or most probable state would possess energy ϵ_i .

It would be useful to introduce a new factor at this point. In a given cell or energy-level i , all the particles may have the same energy ϵ_i , but the energy may be arrayed in different ways for the different particles. When there is a possibility of different ways of array in a state, the state is said to be "degenerate". If there be g_i number of possible distribution of energy in a given energy-level i , then the state is said to be " g_i -degenerate", where g_i is called the statistical weight factor. To illustrate : suppose a cell contains 100 molecules, all of them

having velocity $C = \sqrt{51}$, i.e., $C^2 = 51$. But the velocity components of the different molecules may be different as follows :

($C^2 = C_x^2 + C_y^2 + C_z^2$, where C_x , C_y , C_z are the components in three directions).

	C_x	C_y	C_z	C^2
10 molecules may have	7	1	1	51
15 " " "	1	1	7	51
20 " " "	1	7	1	51
15 " " "	5	5	1	51
20 " " "	5	1	5	51
20 " " "	1	5	5	51

That is, six complexions are possible though the energy-level is the same. The state is then six-fold-degenerate ; statistical weight factor, 6. We can then write equation (VIII.1) and (VIII.2), as

$$\left. \begin{aligned} n_i &= e^{-\alpha} g_i e^{-\beta \epsilon_i} \\ \text{and } n &= e^{-\alpha} \sum g_i e^{-\beta \epsilon_i} \\ \text{and } \frac{n_i}{n} &= \frac{g_i e^{-\beta \epsilon_i}}{\sum g_i e^{-\beta \epsilon_i}} \end{aligned} \right\} \dots \text{(VIII.4)}$$

VIII.3. Partition Function. The denominator $\sum e^{-\beta \epsilon_i}$ in the expression of equation (VIII.3) is a sum of the factor $e^{-\beta \epsilon_i}$ over all the energy-levels. It is called the *partition function* (or (*Zustandssumme*)) and is denoted by f .

$$f = \sum e^{-\beta \epsilon_i},$$

where β is called the modulus of distribution.

The Boltzmann law may then be written as

$$n_i = \frac{n}{f} e^{-\beta \epsilon_i} \dots \text{(VIII.5)}$$

$$\text{i.e., } \ln n_i = \ln n - \ln f - \beta \epsilon_i \dots \text{(VIII.6)}$$

We may now proceed to evaluate β . We have seen that both entropy and probability attain their maximum values when equilibrium is reached. The relation between entropy (S) and probability (W) is

$$S = k \ln W \quad (k, \text{ Boltzmann constant}) \dots \text{(IV.51)}$$

Since W is proportional to the thermodynamic probability (P), we have

$$S - B = k \ln P, \text{ where } B \text{ is a constant.}^*$$

Substituting equations (B) and (VIII.6)

$$\begin{aligned} \frac{S - B}{k} &= n \ln n - \sum n_i \ln n_i \\ &= n \ln n - \sum n_i [\ln n - \ln f - \beta \epsilon_i] \\ &= n \ln n - \ln n \sum n_i + \ln f \cdot \sum n_i + \beta \sum n_i \epsilon_i \\ &= n \ln n - n \ln n + n \ln f + \beta E \quad [\because \sum n_i \epsilon_i = E] \end{aligned}$$

$$\text{or } \frac{S - B}{k} = n \ln f + \beta E \dots \text{(VIII.7)}$$

That is, $S - B = nk \ln f + k\beta E$

$$\text{Differentiating, } \left(\frac{dS}{dE} \right)_v = \frac{nk}{f} \cdot \frac{df}{d\beta} \cdot \left(\frac{d\beta}{dE} \right)_v + k\beta + kE \left(\frac{d\beta}{dE} \right)_v$$

$$\text{Since } f = \sum e^{-\beta \epsilon_i}, \quad \frac{df}{d\beta} = -\sum \epsilon_i e^{-\beta \epsilon_i} = -\frac{E}{n} f.$$

* The constant B has subsequently been taken as zero. (Planck).

$$\therefore \left(\frac{dS}{dE} \right)_v = -\frac{nk}{f} \left(\frac{Ef}{n} \right) \left(\frac{d\beta}{dE} \right)_v + k\beta + kE \left(\frac{d\beta}{dE} \right)_v$$

$$\text{or} \quad \left(\frac{dS}{dE} \right)_v = k\beta$$

When the energy is purely the internal energy, i.e., $E = U$, then

$$\left(\frac{dS}{dU} \right)_v = k\beta$$

But, from the First and Second Laws, $dU + pdv = dQ = TdS$,

$$\text{or} \quad \left(\frac{dS}{dU} \right)_v = \frac{1}{T}$$

$$\text{Hence} \quad k\beta = \frac{1}{T}, \quad \text{or} \quad \beta = \frac{1}{kT} \quad \dots \text{(VIII.8)}$$

$$\text{We may then write the partition function, } f = \sum e^{-\frac{\epsilon_i}{kT}} \quad \dots \text{(VIII.9)}$$

$$\text{and} \quad n_i = \frac{n}{f} e^{-\frac{\epsilon_i}{kT}} \quad \dots \text{(VIII.10)}$$

If the degeneracy of the states are considered, we would have,

$$\left. \begin{aligned} f &= \sum g_i e^{-\frac{\epsilon_i}{kT}} \\ n_i &= \frac{n}{f} \cdot g_i e^{-\frac{\epsilon_i}{kT}} \end{aligned} \right\} \quad \dots \text{(VIII.11)}$$

Qualitatively speaking, the partition function indicates how the particles are distributed among the various energy states. It is a measure of available energy-levels.

VIII.4. Partition Function and Thermodynamic Functions. It is possible to utilise the partition function and the distribution law to evaluate various thermodynamic functions.

(i) **Internal Energy, U .** The internal energy (U) of a system of n molecules (in excess of that at the absolute zero) is given by equation (VIII.10).

$$U = \sum \epsilon_i n_i = \sum \epsilon_i \left(\frac{n}{f} \cdot e^{-\frac{\epsilon_i}{kT}} \right)$$

$$\text{or} \quad U = \frac{n}{f} \sum \epsilon_i e^{-\frac{\epsilon_i}{kT}} \quad \dots \text{(F)}$$

$$\text{But} \quad f = \sum e^{-\frac{\epsilon_i}{kT}} \quad \text{hence} \quad \frac{df}{dT} = \frac{1}{kT^2} \sum \epsilon_i e^{-\frac{\epsilon_i}{kT}}$$

$$\text{or} \quad \sum \epsilon_i e^{-\frac{\epsilon_i}{kT}} = kT^2 \frac{df}{dT}$$

Substituting in eqn. (F) above, the internal energy,

$$U = \frac{n}{f} \sum \epsilon_i e^{-\frac{\epsilon_i}{kT}} = \frac{nkT^2}{f} \frac{df}{dT} = nkT^2 \frac{d \ln f}{dT} \quad \dots \text{(VIII.12)}$$

For a gm-mole, $U = N_0 k T^2 \frac{d \ln f}{dT}$, where N_0 = Avogadro number.

The average energy of each molecule, $\epsilon = k T^2 \frac{d \ln f}{dT}$. . . (VIII.13)

(ii) **Entropy, S.** From equation (VIII.7) assuming the constant $B = 0$ (Planck's arbitrary assumption), we have

$$S = nk \ln f + k \beta U$$

Since $\beta = \frac{1}{kT}$, we have $S = nk \ln f + \frac{U}{T}$. . . (VIII.14)

Substituting U by equation (VIII.12)

$$S = nk \ln f + nkT \frac{d \ln f}{dT} \quad \dots (VIII.15)$$

(iii) **Free Energy, F.** We know free energy is defined as $F = U - TS$. Since U and S can be expressed in terms of partition function f , using equation (VIII.14),

$$F = U - T \left[nk \ln f + \frac{U}{T} \right]$$

or $F = -nkT \ln f$. . . (VIII.16)

(iv) **Pressure, P.** The free-energy change is given by

$$\Delta F = -P \Delta V + S \Delta T$$

or $P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F}{\partial f}\right)_T \left(\frac{\partial f}{\partial V}\right)_T$

Since $F = -nkT \ln f$, $\left(\frac{\partial F}{\partial f}\right)_T = -\frac{nkT}{f}$

$\therefore P = \frac{nkT}{f} \left(\frac{\partial f}{\partial V}\right)_T = nkT \left(\frac{\partial \ln f}{\partial V}\right)_T$. . . (VIII.17)

(v) **Gibb's Potential, G.** Since $G = F + PV$, we can write

$$G = -nkT \ln f + nkT \left(\frac{\partial \ln f}{\partial V}\right)_T \cdot V$$

or $G = -nkT \left[\ln f - \left(\frac{\partial \ln f}{\partial \ln V}\right)_T \right]$. . . (VIII.18)

(vi) **Heat Content, H.** The heat content, $H = U + PV$. Substituting with equations (VIII.12) and (VIII.17).

$$H = nkT^2 \frac{d \ln f}{dT} + nkT \left(\frac{d \ln f}{dV}\right)_T \cdot V$$

or $H = nkT \left[\left(\frac{d \ln f}{d \ln T}\right) + \left(\frac{d \ln f}{d \ln V}\right)_T \right]$. . . (VIII.19)

(vii) **Heat Capacity, C_v.** By definition, $C_v = \left(\frac{dU}{dT}\right)_V$.

Hence $C_v = nk \frac{d}{dT} \left(\frac{T^2 d \ln f}{dT} \right)$. . . (VIII.20)

VIII.5. Molar Partition Function. So far we have considered systems in which there were n individual distinguishable particles distributed in different energy-levels and f denoted the *molecular partition function*. But we have to deal with large-scale systems. in which quantities are taken in gm-moles.

Let us now take a system which may be supposed to be constituted of large number of smaller ones each with a gm-mole of the substance. That is, the individual unit here is not the molecule but a *mole*. Let the energy-levels allowed for the whole system be $E_1, E_2, \dots E_t \dots$, and let there be x such systems in all. In each of these there are, of course, N_0 , Avogadro number of molecules. Then, the average energy E , of such a unit is

$$E = \frac{\sum x_t E_t}{\sum x_t}$$

If Z be the partition function of these systems, then $Z = \sum e^{-\frac{E_t}{kT}}$

Now, following the procedure as in the previous section (equation VIII.13),

$$E = kT^2 \left[\frac{d \ln Z}{dT} \right] \quad \dots \text{(VIII.21)}$$

where we designate Z as the *molar partition function*.

But we know, (eqn. VIII.12) the energy of a gm-mole, [for convenience of writing, Avogadro number N_0 is written as N],

$$E = NkT^2 \left[\frac{d \ln f}{dT} \right] = kT^2 \left[\frac{d \ln f^N}{dT} \right]$$

This leads, on comparison, to the result, $Z = f^N$.

The thermodynamic functions may then be written, as,

$$\left. \begin{aligned} (a) \quad S &= NkT \frac{d \ln f}{dT} + Nk \ln f \\ &= kT \frac{d \ln Z}{dT} + k \ln Z \\ (b) \quad F &= -NkT \ln f = -kT \ln Z \\ (c) \quad G &= -NkT \left[\ln f - \left(\frac{d \ln f}{d \ln V} \right)_T \right] \\ &= -kT \left[\ln Z - \left(\frac{d \ln Z}{d \ln V} \right)_T \right] \end{aligned} \right\} \quad \dots \text{(VIII.22)}$$

These relations would be true for systems where the molecules are all distinguishable and can occupy energy-levels without any restriction. Thus, these expressions would be valid, say, in the case of a crystal where the different atoms occupy fixed localised positions in the structure.

But in the case of indistinguishable particles, there would be some difference. We may proceed to consider it in the following fashion.

Suppose there are two distinguishable particles (a, b) which may be in three possible energy-levels ($\epsilon_1, \epsilon_2, \epsilon_3$). Then the energy of the system may give rise to the following nine distributions,

$$\begin{array}{lll} (i) \quad E_1 = \epsilon_1(a) + \epsilon_1(b) & (iv) \quad E_4 = \epsilon_1(a) + \epsilon_2(b) & (vii) \quad E_7 = \epsilon_1(b) + \epsilon_2(a) \\ (ii) \quad E_2 = \epsilon_2(a) + \epsilon_2(b) & (v) \quad E_5 = \epsilon_1(a) + \epsilon_3(b) & (viii) \quad E_8 = \epsilon_1(b) + \epsilon_3(a) \\ (iii) \quad E_3 = \epsilon_3(a) + \epsilon_3(b) & (vi) \quad E_6 = \epsilon_2(a) + \epsilon_3(b) & (ix) \quad E_9 = \epsilon_2(b) + \epsilon_3(a) \end{array}$$

Then, $Z = e^{-2\epsilon_1/kT} + e^{-2\epsilon_2/kT} + e^{-2\epsilon_3/kT} + 2e^{-\epsilon_1/kT} \cdot e^{-\epsilon_2/kT}$

$$+ 2e^{-\epsilon_1/kT} \cdot e^{-\epsilon_3/kT} + 2e^{-\epsilon_2/kT} \cdot e^{-\epsilon_3/kT}$$

$$= [e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT} + e^{-\epsilon_3/kT}]^2 = [\sum e^{-\epsilon_i/kT}]^2 = f^2$$

Now if the system contains N molecules (1 mole), then

$$\begin{aligned} Z &= [\sum e^{-E_i/kT}] = \sum e^{-(\epsilon_1 + \epsilon_2 + \dots + \epsilon_1 + \dots + \epsilon_N)/kT} \\ &= \sum e^{-\epsilon_1/kT} \cdot e^{-\epsilon_2/kT} \dots e^{-\epsilon_N/kT} \end{aligned}$$

(since each of these have N possible energy-levels),

$$\text{or} \quad Z = (\sum e^{-\epsilon/kT})^N = f^N \quad \dots \text{(VIII.23)}$$

This is the result obtained earlier.

But if we presume the molecules to be indistinguishable, as in the case of a *perfect gas*, the relation above requires modification, for we have taken too many possible arrangements of the particles. In the case cited above, the state (iv) will be the same as (vii), when 'a' and 'b' are identical. So the number of distribution would be much less. The N -particles in a gm-mole are all indistinguishable and these had $N!$ permutations among themselves in as many energy levels. We should therefore reduce the expression for Z by dividing the same with $N!$. Hence, for indistinguishable particles (a perfect gas), the molar partition function, Z in eqn. VIII.22 should be replaced by $Z/N!$

It is obvious that for systems of real gases, liquids, etc. such rigid relations will not be valid. For a perfect gas, the thermodynamic functions shall be, [see equation VIII.22]

$$\left. \begin{aligned} (a) \quad S &= k \ln \left(\frac{Z}{N!} \right) + kT \frac{d}{dT} \left(\ln \frac{Z}{N!} \right) \\ &= k \ln Z + kT \frac{d \ln Z}{dT} - k \ln N! \\ (b) \quad F &= -kT \ln \frac{Z}{N!} = -kT \ln Z + kT \ln N! \\ &= -kT \ln Z + NkT \ln N - NkT \\ &= -RT \left[\ln \frac{f}{N} + 1 \right] \\ (c) \quad G &= F + PV = F + RT = -RT \ln \frac{f}{N} \end{aligned} \right\} \dots \text{(VIII.24)}$$

VIII.6. The Third Law. It is now possible to make a statistical formulation of the Third Law. We have seen in section IX.5,

$$S_T - S_0 = \int_0^T \frac{C_p}{T} dT$$

$$\text{At very low temperatures, } S_T - S_0 = \int_0^T \frac{C_v}{T} dT \quad (\because C_p \approx C_v)$$

Substituting partition function expression for C_v ,

$$\begin{aligned} S_T - S_0 &= \int_0^T \frac{1}{T} \left(\frac{dU}{dT} \right)_v dT \\ &= \int_0^T \frac{1}{T} \frac{d}{dT} \left(kT^2 \frac{\partial \ln Z}{\partial T} \right)_v dT \end{aligned}$$

$$\begin{aligned}
 &= kT \left(\frac{d \ln Z}{dT} \right)_V + k \int_0^T \left(\frac{d \ln Z}{dT} \right)_V dT \\
 &= \frac{U}{T} + k \ln (Z)_T - k \ln (Z)_0
 \end{aligned}$$

Equating the temperature-independent terms, we find

$$S_0 = k \ln (Z)_0 = k \ln (f^N)_0 = R \ln (f)_0 = R \ln (g_0 e^0) = R \ln g_0$$

where g_0 is the statistical weight factor of the lowest energy state. In a perfect crystal at 0°K , there is only one arrangement, which means $g_0 = 1$; hence the entropy $S_0 = 0$, which is the Third Law.

VIII.7. Partition Function for Molecules with Different Types of Energy. It is a fact that most often the molecules are associated with energy of different types. In expressing the partition function, all the types of energy have to be considered. Take a system containing N molecules (all of the same kind), all possessing different kinds of energy, say, translational, vibrational, rotational etc. Let the different types of energy be labelled $\alpha, \beta, \gamma, \dots$ etc.

The allowed energy-levels of the α -type are $\epsilon_{\alpha_1}, \epsilon_{\alpha_2}, \epsilon_{\alpha_3}, \dots$,

for β -type are $\epsilon_{\beta_1}, \epsilon_{\beta_2}, \epsilon_{\beta_3}, \dots$, and so on.

The respective Boltzmann distributions will be

$$N_i^\alpha = \frac{N}{f_\alpha} e^{-\epsilon_{\alpha_i}/kT}, N_i^\beta = \frac{N}{f_\beta} e^{-\epsilon_{\beta_i}/kT}, \dots$$

where $f_\alpha, f_\beta, \dots$ etc., are the partition functions appropriate to $\alpha, \beta, \dots$ types of energy.

The total energy (E) of the system is

$$\begin{aligned}
 E &= \sum \epsilon_{\alpha_i} \cdot N_i^\alpha + \sum \epsilon_{\beta_i} N_i^\beta + \sum \epsilon_{\gamma_i} N_i^\gamma + \dots \\
 &= NkT^2 \frac{\partial}{\partial T} \ln f_\alpha + NkT^2 \frac{\partial}{\partial T} \ln f_\beta + NkT^2 \frac{\partial}{\partial T} \ln f_\gamma + \dots \\
 &= NkT^2 \frac{\partial}{\partial T} \ln (f_\alpha f_\beta f_\gamma \dots).
 \end{aligned}$$

If f is the net molecular partition function, when every molecule is capable of freely taking any number of types of energy, we may write,

$$E = NkT^2 \frac{\partial}{\partial T} \ln f.$$

Comparing,

$$f = f_\alpha \cdot f_\beta \cdot f_\gamma \dots$$

$\dots$ (VIII.25)

i.e., the net partition function is the product of the separate partition functions in respect of different types of energy associated with the molecules.

VIII.8. Partition Function for Translational Energy. The translational energy is also quantised, though the difference in the energy-levels are quite small. The only way in which a particle would exhibit periodicity in translational motion is in relation to its impacts on the walls of the container. Suppose in a cubical box of length l , a molecule is moving parallel to x -axis and repeats its motion each time it completes a path $2l$. Then $2l = n\lambda$, where n is an integer and λ is the wavelength associated with the matter-wave. The translational energy (ϵ_x) along the x -axis is given by,

$$\epsilon_x = \frac{1}{2} mc_x^2 = \frac{1}{2m} \cdot p^2 \quad (p, \text{ the momentum})$$

$$\begin{aligned} \text{or} \quad \epsilon_x &= \frac{1}{2m} \left(\frac{h}{\lambda} \right)^2 && \text{(using de-Broglie relation)} \\ &= \frac{1}{2m} \left(\frac{hn}{2l} \right)^2 = \frac{n^2 h^2}{8ml^2} \end{aligned}$$

The molecular partition function due to translation in x -direction,

$$f_x = \sum e^{-\epsilon_x/kT} = \sum e^{-\frac{n^2 h^2 / 8ml^2}{kT}}$$

Since energy levels are very close, we may assume continuity, so that

$$f_x = \int_0^\infty e^{-\frac{n^2 h^2 / 8ml^2}{kT}} dn$$

$$\text{Put } \frac{n^2 h^2}{8ml^2 kT} = a^2, \text{ so that } dn = \frac{l}{h} (8mkT)^{\frac{1}{2}} da$$

$$\begin{aligned} \text{Hence } f_x &= \frac{(8mkT)^{\frac{1}{2}} l}{h} \int_0^\infty e^{-a^2} da \\ &= \frac{(8mkT)^{\frac{1}{2}} l}{h} \cdot \sqrt{\frac{\pi}{4}} = \frac{(2\pi mkT)^{\frac{1}{2}} l}{h} \quad (\text{app. I.3}) \end{aligned}$$

When we consider the translational motion in all the three directions, the molecular partition function for translation would be

$$f = f_x^3 = \frac{(2\pi mkT)^{3/2} l^3}{h^3} = \frac{(2\pi mkT)^{3/2} V}{h^3} \quad \dots (\text{VIII.26})$$

In the case of a perfect monatomic gas, the molar partition function,

$$\begin{aligned} Z &= \frac{f^N}{N!} = \frac{1}{N!} \left[\frac{(2\pi mkT)^{3/2} V}{h^3} \right]^N \\ &= \left(\frac{e}{N} \right)^N \left[\frac{(2\pi mkT)^{3/2} V}{h^3} \right]^N \left[\because \text{Stirling's } N! = \left(\frac{N}{e} \right)^N \right] \\ &= \left[\frac{(2\pi mkT)^{3/2} V e}{N h^3} \right]^N \quad \dots (\text{VIII.27}) \end{aligned}$$

$$\text{or } \ln Z = N \ln \frac{(2\pi mkT)^{3/2} V e}{N h^3} \quad \dots (\text{VIII.28})$$

(i) The internal energy of a monatomic gas may be obtained directly now, as the vibrational and rotational energies are absent.*

$$U = kT^2 \frac{d \ln Z}{dT} = NkT^2 \frac{d \ln f}{dT} = RT^2 \left(\frac{3}{2} \cdot \frac{1}{T} \right) = \frac{3}{2} RT$$

(ii) The entropy of the monatomic gas or vapour can also be evaluated.

$$\begin{aligned} S &= \frac{U}{T} + k \ln Z \\ &= \frac{3}{2} R + Nk \ln \frac{(2\pi mkT)^{3/2} V e}{N h^3} \quad (\text{neglecting statistical weight factor}) \\ &= R \ln \frac{(2\pi mkT)^{3/2} V e^{5/2}}{N h^3} \quad \dots (\text{VIII.29}) \end{aligned}$$

* From eqn. VIII.26, $\ln f = \ln \frac{(2\pi mk)^{3/2} V}{h^3} + \ln T^{3/2}$ or $\frac{\partial \ln f}{\partial T} = \frac{3}{2} \cdot \frac{1}{T}$

From eqn. (VIII.36), $E_v = \frac{N h \nu}{2} + N h \nu \cdot e^{-h \nu / k T} \left(1 - e^{-h \nu / k T} \right)^{-1}$

$$\therefore U = \frac{5}{2} N k T + \frac{1}{2} N h \nu + \frac{N h \nu}{(e^{h \nu / k T} - 1)} \quad \dots \text{(VIII.38)}$$

(ii) Heat Capacity, C_V

$$C_V = \left(\frac{dU}{dT} \right)_V = \frac{5}{2} N k + N k \left(\frac{h \nu}{k T} \right)^2 \cdot \frac{e^{h \nu / k T}}{(e^{h \nu / k T} - 1)^2} \quad \dots \text{(VIII.39)}$$

(iii) Entropy, S [from equations (VIII.31, 34, 36)] and using $S = k \ln Z$,

$$\begin{aligned} S = R \ln \frac{(2\pi)^{3/2} (ek)^{7/2} \cdot 8\pi^2 I}{N^{3/2} h^5 o} + \frac{7}{2} R \ln T + \frac{3}{2} R \ln M - R \ln P \\ + \frac{N h \nu}{T} (e^{h \nu / k T} - 1)^{-1} - N k \ln (1 - e^{-h \nu / k T}). \quad \dots \text{(VIII.40)} \end{aligned}$$

VIII.11. Heat Capacity of Solids. We can also employ partition functions in the evaluation of heat-capacity of solids, as proposed by Debye. Debye suggested (see also Sec. III.16) that the atoms were vibrating with a spectrum of modes of vibration ranging from ν_0 (ground state) to ν_m , some maximum frequency. The range is large enough to assume ν_0 to be practically zero. The modes of vibration are limited in number.

We have seen in (eqn. III.9) that the modes of vibration for a radiation between ν and $\nu + \Delta \nu$ in volume V is given by, $dn = \frac{4\pi V}{C^3} \nu^2 d\nu$.

Applying the same considerations to crystals and remembering that in this case, there would be three possible directions of propagation—two transverse and one longitudinal—we may write,

$$dn = \frac{12\pi V}{C^3} \nu^2 d\nu,$$

where C is the average velocity of elastic waves in the crystal.

The total modes of vibration in the crystal is $3N$. Hence,

$$\int_0^{\nu_m} \frac{12\pi V}{C^3} \nu^2 d\nu = 3N$$

$$\text{or } \nu_m^3 = \frac{3}{4\pi} \cdot \frac{N C^3}{V} \quad \dots \text{(a)}$$

$$\therefore \frac{V}{C^3} = \frac{3N}{4\pi \nu_m^3}$$

$$\text{We may therefore write, } \phi(\nu) = 12\pi \cdot \frac{3N}{4\pi \nu_m^3} \cdot \nu^2 = \frac{9N}{\nu_m^3} \nu^2 \quad \dots \text{(}\beta\text{)}$$

Again, the atomic partition function (vibrational) is

$$f = e^{-h \nu / k T} (1 - e^{-h \nu / k T})^{-1}$$

or

$$\ln f = -\frac{1}{2} \frac{h \nu}{k T} - \ln (1 - e^{-h \nu / k T})$$

The partition function of the whole crystal may be obtained by attaching to each frequency the partition function of the single oscillation, *i.e.*,

$$\begin{aligned} N \ln f &= \int_0^{v_m} \phi(v) \left[-\frac{1}{2} h v / k T - \ln (1 - e^{-h v / k T}) \right] dv \\ &= \frac{9N}{v_m^3} \int_0^{v_m} \left[-\frac{1}{2} h v / k T - \ln (1 - e^{-h v / k T}) \right] v^2 dv \\ &= -\frac{9}{8} \frac{N h v_m}{k T} - 3N \ln (1 - e^{-h v_m / k T}) + \frac{3N}{v_m^3} \int_0^{v_m} \frac{h v^3}{k T} \frac{e^{-h v / k T}}{1 - e^{-h v / k T}} dv \end{aligned}$$

At sufficiently low temperature, the second term is very small and negligible.

Putting $\frac{h v}{k T} = x$, we find,

$$\begin{aligned} N \ln f &= -\frac{9}{8} \frac{N h v_m}{k T} + 3N \left(\frac{k T}{h v_m} \right)^3 \int \frac{x^3}{e^x - 1} dx \\ &= -\frac{9}{8} \frac{N h v_m}{k T} + 3N \cdot \left(\frac{k T}{h v_m} \right)^3 \cdot \frac{\pi^4}{15} \end{aligned}$$

Now, substituting this in equation (VIII.12), the energy is

$$E = \frac{9}{8} N h v_m + \frac{3\pi^4}{5} N k \cdot \left(\frac{k}{h v_m} \right)^3 T^4$$

Therefore, the heat-capacity would be,

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{12\pi^4}{5} N k \left(\frac{k}{h v_m} \right)^3 T^3 \quad \dots \text{(VIII.41)}$$

This is Debye's specific-heat relation at low temperatures. Expressing

$\frac{h v_m}{k} = \theta_D$, the equation may be written as

$$C_V = \frac{12\pi^4}{5} \cdot R \cdot \frac{T^3}{\theta_D^3} = \frac{464.6}{\theta_D^3} \cdot T^3$$

It is the same relation as obtained in (III.14).

VIII.12. Quantum Statistics. We have so far attempted to predict the behaviour and properties of systems from the Boltzmann statistics, also often called the 'classical' statistics. The classical statistics apply to crystalline solids fairly well. At low densities of gases, the Boltzmann distribution law is satisfactory, but when the density is high, the classical statistics shows little agreement with experimental facts. To illustrate, the energy of a photon is proportional to its frequency. From classical statistics we have the energy distribution, which gives us the distribution of frequency. As the frequency increases, according to classical statistics, there would be a continuous increase in the no. of photons per unit range of frequency. But we know that there is a maximum in the actual distribution. In the same way, the classical statistics failed also to explain the behaviour of 'electron-gas' in the conductors. These anomalies led to the formulation of quantum statistics developed in two ways for different systems—(i) Bose-Einstein statistics and (ii) Fermi-Dirac statistics. It will be seen later that the Boltzmann distribution law follows from either the B-E statistics or the F-D statistics, provided the density of the material is comparatively low. For real gases, at ordinary pressures, corrections with any quantum statistics are quite small and Boltzmann statistics would be appropriate enough.

VIII.13. The Bose-Einstein Statistics. In classical distribution the particles are labelled, *i.e.*, distinguished from one another. If two particles interchange their positions (or energy states), a new complexion would occur. But in Bose-Einstein statistics, we start with identical particles

which are indistinguishable. Thus, the interchange of two particles between two energy-states will not give rise to a new complexion or macrostate.

On the assumption and following the procedure adopted in Boltzmann statistics, it can be shown, the actual number in which n_i particles may be allocated in p_i states is given by

$$\frac{(n_i + p_i - 1)}{n_i! (p_i - 1)!}, \text{ or } P = \prod \frac{(n_i + p_i - 1)}{n_i! (p_i - 1)!}$$

$$\text{whence } n_i = \frac{p_i}{e^{\alpha} e^{\beta \epsilon_i} - 1}$$

This is *Bose-Einstein Distribution Law*.

VIII.14. The Fermi-Dirac Statistics. In the Boltzmann or in the Bose-Einstein statistics, there was no restriction as to the number of particles present in any energy-state. But in applying the distribution law to particles, like electrons, the Pauli Exclusion principle is invoked. That is, two particles in an atom cannot have the same energy-state. It means that not more than one particle can be assigned to a particular energy-state.

Let there be n_i particles of energy ϵ_i in which there are p_i energy-states. Remembering that all particles are identical and that one state can have only one particle, the number of ways n_i particles can be distributed amongst p_i states in that group is given by,

$$\frac{p_i!}{n_i! (p_i - n_i)!}$$

$$\text{The thermodynamic probability will be, } P = \prod \frac{p_i!}{n_i! (p_i - n_i)!}$$

taking into consideration all the groups in the macroscopic state,

$$\text{whence } n_i = \frac{p_i}{e^{\alpha} e^{\beta \epsilon_i} + 1}$$

which is the *Fermi-Dirac Distribution Law*.

When α or ϵ_i is large, both the Bose-Einstein or the Fermi-Dirac distributions are rendered into

$$n_i = p_i e^{-\alpha} e^{-\beta \epsilon_i}$$

which is the same as the Boltzmann distribution (eqn. VIII.4).

Reference for further reading

1. *Thermodynamics and statistical mechanics*—ASTON and FRITZ
2. *Introduction to statistical mechanics* : RUSHBROOKE
3. *Statistical mechanics* : MAYER & MAYER

Exercise -

1. Using partition function, show that for a monatomic gas,
 $E = \frac{3}{2} NkT$, $p = NkT/V$.
2. Explain clearly the terms 'molecular' and 'molar' partition functions. Show how the eqm. constant of a reaction can be calculated from a knowledge of the partition functions of the reacting species.
3. Compute the translational entropy of a mole of a monatomic gas at 1 atm as a function of M and T from partition function. Evaluate the expression for argon at 27°C ($M = 40$).
4. Calculate the value of the classical rotational partition function for carbon monoxide at 20°C. The internuclear distance, $r = 1.1282 \text{ \AA}$; the atomic masses are C = 12.00390, O = 16.00000.

$$[\text{Hint : } I = \mu r^2 = \frac{12.00390 + 16.00000}{28.00390} \times \frac{1}{6 \times 10^{23}} \times 1.1282^2 \times 10^{-16}]$$

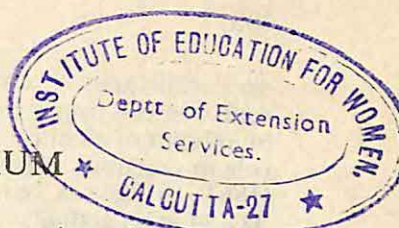
$$= 14.49 \times 10^{-40} \text{ g-cm}^2/\text{molecule.}$$

$$f_r = \frac{8\pi^2 I k T}{h^2}$$

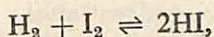
[Ans. 7.11940]

5. Discuss the attempts which have been made to account quantitatively for the variation of atomic heat of solids with temperature.

THE CHEMICAL EQUILIBRIUM



IX.1. Equilibrium. It is common knowledge that many reactions do not go to completion even if favourable external conditions are maintained. The reactions proceed to some extent and then they come to a stop. A portion of the reactants, sometimes a considerable portion, remain unaltered in the system. For example, in the reaction,



if some hydrogen and iodine vapour be kept at a constant temperature in a closed vessel, only a portion of these will be converted into hydrogen iodide, and then the reaction would stop. A mixture of hydrogen iodide, iodine and hydrogen will remain in the vessel for unlimited time, temperature being kept constant. On the other hand, if at the same temperature, some hydrogen iodide be taken in a closed vessel, a fraction will decompose into hydrogen and iodine and the rest of hydrogen iodide will remain intact. The proportions of hydrogen, iodine and hydrogen iodide in the mixture will be the same in both the experiments. When such a stage is reached in the course of a reaction that no further action is apparent, it is said to have attained equilibrium at that temperature. It is obvious that the reaction can proceed either way and the composition of the system at eqm. is fixed. The cessation of chemical reaction is however only apparent. In fact, when equilibrium is attained, the reactions proceed in both directions at equal rates, so that the amount of reactants disappearing per unit time is reproduced from the action in opposite direction. The equilibrium is thus really a dynamic one, not static. The reactions proceeding in both directions are called "*reversible reactions*". It is very likely that all chemical reactions are reversible. But in some cases, the extent of opposite reaction is so small as to be negligible and such reactions are said to proceed to completion in one direction. In such cases, really the point of equilibrium is attained at an extreme end of the concentrations of the resultants, the concentration of unreacted materials being extremely small to be detected.

IX.2. The Law of Mass Action. There is another aspect of the chemical reactions which attracted the interest of the chemists from very early days. This is about the causes as to why two substances react and undergo a chemical change. Even in the eighteenth century, it was only empirically stated that chemical action resulted from an affinity between the reacting substances. But no precise meaning of affinity was clearly conceived. In 1777, Wenzel from an investigation of the action of acids on metals concluded that the rate of dissolution of metals, which is a measure of affinity of the process, is proportional to the amount of acid present in a given volume. In 1799, Berthollet explained the formation of huge deposits of sodium carbonate in some Egyptian lakes due to the reaction, $2\text{NaCl} + \text{CaCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CaCl}_2$. But in the laboratory, the reaction proceeds exactly in the opposite way. Calcium carbonate is precipitated from addition of calcium chloride to sodium carbonate. Berthollet suggested that the opposite process of formation of sodium carbonate was possible due to the very heavy concentration of sodium chloride there. Berthollet thus not only introduced the idea of reversibility in chemical processes, but also pointed out the role the concentration might play in directing the course of a reaction. Berthollet however made an error in suggesting further that the composition of the resultant compound would also be affected by the amount of the reactant present. This was contrary to the law of constant proportion which was also simultaneously firmly established. As a result, Berthollet's ideas were wholly rejected and for a long time there had been very little progress. In 1850, Wilhelmy investigated the rates of inversion of sugars and found that these rates are directly related to the amounts of sugar present per unit volume. In 1862, Berthelot and St. Gilles studied the formation of ester from ethyl alcohol

Activities are related to concentration units as $a = \gamma_N N$, or $a = f.C$, where γ_N and f are the activity coefficients and N and C are the concentrations in mole-fraction and molarity basis respectively at equilibrium.

Substituting these in equation (IX.3) we get,

$$(i) \quad \frac{N_D^d \times N_E^e \times N_F^f \times \dots}{N_A^a \times N_B^b \times N_C^c \times \dots} \times \frac{\gamma_{ND}^d \times \gamma_{NE}^e \times \gamma_{NF}^f \times \dots}{\gamma_{NA}^a \times \gamma_{NB}^b \times \gamma_{NC}^c \times \dots} = K_a \quad \dots (IX.4)$$

$$(ii) \quad \frac{C_D^d \times C_E^e \times C_F^f \times \dots}{C_A^a \times C_B^b \times C_C^c \times \dots} \times \frac{f_D^d \times f_E^e \times f_F^f \times \dots}{f_A^a \times f_B^b \times f_C^c \times \dots} = K_a \quad \dots (IX.5)$$

In ideal systems, the activity coefficients are equal to unity. For practical purposes in approximate valuations, dilute solutions or gas-mixtures are supposed to behave almost ideally. In such circumstances, equation (IX.5) may be written as,

$$\frac{C_D^d \times C_E^e \times C_F^f \times \dots}{C_A^a \times C_B^b \times C_C^c \times \dots} = K_a = K_C \text{ (say)} \quad \dots (IX.6)$$

This relation is the same as derived in (IX.2); K_C is the equilibrium constant expressed in terms of molar units of concentration of the components where the system behaves almost ideally. Thus we see, the expression for eqm. constant is a consequence of the laws of thermodynamics, independent of the rates of opposite reactions.

Gaseous reactions. In a gaseous reaction, components are usually expressed in terms of their partial pressures instead of molarities. If the gases are supposed to behave ideally, we have the activities equal to the fugacities. Further, the fugacities may be replaced by the partial pressures of the components, such as P_A , P_B , ... P_D , P_E , ... etc.

Then the total pressure,

$$P = P_A + P_B + \dots + P_D + P_E + \dots$$

The equilibrium constant, K_a , is given by,

$$K_a = \frac{a_D^d \times a_E^e \times \dots}{a_A^a \times a_B^b \times \dots}$$

Then, in terms of fugacities,

$$K_f = \frac{f_D^d \times f_E^e \times \dots}{f_A^a \times f_B^b \times \dots}$$

So, in terms of pressure the equilibrium constant, called K_P , is given by

$$K_P = \frac{P_D^d \times P_E^e \times \dots}{P_A^a \times P_B^b \times \dots} \quad \dots (IX.7)$$

Again, assuming ideality, we can express pressures as

$$P_A = C_A RT, \quad P_B = C_B RT, \text{ etc. Hence,}$$

$$\begin{aligned} K_P &= \frac{(C_D RT)^d \times (C_E RT)^e \times \dots}{(C_A RT)^a \times (C_B RT)^b \times \dots} \\ &= \frac{C_D^d \times C_E^e \times \dots}{C_A^a \times C_B^b \times \dots} \times (RT)^{d+e-\dots-a-b-\dots} \end{aligned}$$

$$\text{or,} \quad K_P = K_C (RT)^{\Delta v} \quad \dots (IX.8)$$

in which Δv = no. of resultant molecules — no. of reactant molecules. It is a relation between the equilibrium constants derived from partial pressure units and from molar concentration units of components.

We can also write the partial pressure in terms of mol-fractions (N), so that $P_A = N_A P$, $P_B = N_B P$, etc.

Then,

$$K_P = \frac{(N_D \cdot P)^d \times (N_E \cdot P)^e \times \dots}{(N_A \cdot P)^a \times (N_B \cdot P)^b \times \dots}$$

$$= \frac{N_D^d \times N_E^e \times \dots}{N_A^a \times N_B^b \times \dots} \cdot P^{(d+e+\dots-a-b-\dots)}$$

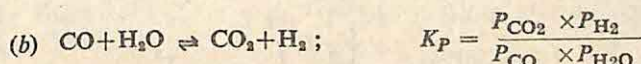
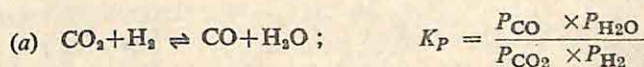
or $K_P = K_N \cdot P^{\Delta v} \quad \dots (IX.9)$

A special feature regarding these equilibrium constants should be mentioned here. At any given temperature, the value of K_P or K_C is independent of pressure and does not change either with total pressure or partial pressure variations. But this is not true of K_N . For,

$$K_N = K_P \cdot \frac{1}{P^{\Delta v}}$$

The relation involves the total pressure P , so the magnitude of K_N would vary with the pressure except when $\Delta v = 0$.

It is a common convention to write the equilibrium constant with the concentrations (or activities) of the resultants in the numerator and those of the reactants in the denominator. To illustrate,



Hence, $K_{\text{forward process}} = \frac{1}{K_{\text{reverse process}}}$

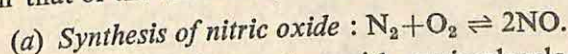
IX.4. Equilibrium Constants of Some Typical Reactions

GASEOUS SYSTEMS

In the study of equilibria, gas reactions are broadly classified into two groups :

(i) *First type gas reactions* in which total number of reactant molecules and of resultant molecules are the same, i.e., $\Delta v = 0$, e.g., $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$

(ii) *Second type gas reactions* in which the number of molecules of reactants differ from that of the resultants, i.e., $\Delta v \neq 0$; e.g., $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$



Suppose initially we start with equimolecular proportion of Nitrogen and Oxygen and if a gm-moles out of each gm-mole react to form nitric oxide at equilibrium, then their relative amounts would be

	N_2	O_2	NO	Total
Moles :	$1-a$	$1-a$	$2a$	$= 2$
Partial Pressures :	$\frac{1-a}{2} P$	$\frac{1-a}{2} P$	$\frac{2a}{2} P$	$= P$
Concentrations :	$\frac{1-a}{V}$	$\frac{1-a}{V}$	$\frac{2a}{V}$	$= \frac{2}{V}$

where V is the volume of the system at eqm. when 1 mole of each of the reactants was originally taken and total pressure is P . Then

$$K_P = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} \cdot P_{\text{O}_2}} = \frac{\left(\frac{2a}{2}P\right)^2}{\left(\frac{1-a}{2}P\right)^2} = \frac{4a^2}{(1-a)^2}$$

and

$$K_C = \frac{C_{\text{NO}}^2}{C_{\text{N}_2} \cdot C_{\text{O}_2}} = \frac{(2a/V)^2}{\left(\frac{1-a}{V}\right)^2} = \frac{4a^2}{(1-a)^2}$$

Thus, K_P and K_C are the same, and are independent of pressure or volume. This is true of all 1st type gas reactions.

When a is small, $4a^2 \approx K_P$ or $a = \frac{1}{2} K_P^{\frac{1}{2}}$.

The extent of the reaction at eqm. can be obtained from K_P .

(b) *Water gas reaction* : $\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}$.

This is also a 1st type gas reaction. Starting with equimolecular mixture of the reactants, we have, when x is the extent of H_2 used up at eqm.

	H_2	CO_2	H_2O	CO	Total
Moles at eqm. :	$1-x$	$1-x$	x	x	$= 2$
Partial Pressures :	$\frac{1-x}{2}P$	$\frac{1-x}{2}P$	$\frac{x}{2}P$	$\frac{x}{2}P$	$= P$

$$K_P = \frac{P_{\text{H}_2\text{O}} \times P_{\text{CO}}}{P_{\text{H}_2} \times P_{\text{CO}_2}} = \frac{\left(\frac{x}{2}P\right)^2}{\left(\frac{1-x}{2}P\right)^2} = \frac{x^2}{(1-x)^2}$$

x is independent of pressure.

At 1260°K and 1 atmosphere, the eqm. composition of this reaction is $\text{CO}_2 = 21.4$, $\text{H}_2 = 22.9$ and $\text{CO} = 27.8$ (moles per cent).

Hence

$$K_P = \frac{P_{\text{H}_2\text{O}} \times P_{\text{CO}}}{P_{\text{CO}_2} \times P_{\text{H}_2}} = \frac{(27.8)^2}{(21.4) \times (22.9)} = 1.58$$

It is often difficult to estimate x directly in this system, and an indirect method is employed. The eqm. constant is computed from the known values of eqm. constants of other reactions. Consider two other equilibria :

(i) $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$; $K_1 = \frac{P_{\text{CO}}^2 \times P_{\text{O}_2}}{P_{\text{CO}_2}^2}$

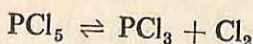
(ii) $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$; $K_2 = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 \times P_{\text{O}_2}}$

So,

$$K_1 \times K_2 = \left[\frac{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}{P_{\text{H}_2} \times P_{\text{CO}_2}} \right]^2 = K_P^2$$

Since K_1 and K_2 can both be separately determined, K_P is known.

(c) We may now consider some 2nd type gas reactions. such as the *dissociation of phosphorus pentachloride* :



Let us start with a gm-mole of PCl_5 and suppose the degree of dissociation is a

at equilibrium. Then, the relative amounts of the components and their pressures would be :

	PCl_5	PCl_3	Cl_2	Total
Moles	$1-a$	a	a	$= 1+a$
Partial pressures	$\frac{1-a}{1+a} P$	$\frac{a}{1+a} P$	$\frac{a}{1+a} P$	$= P$
Concentrations	$\frac{1-a}{V}$	$\frac{a}{V}$	$\frac{a}{V}$	$= \frac{1+a}{V}$

V , the volume of the system.

$$\text{Hence, } K_P = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{\left(\frac{a}{1+a} P\right) \left(\frac{a}{1+a} P\right)}{\frac{1-a}{1+a} P} = \frac{a^2}{1-a^2} P.$$

$$\text{and } K_C = \frac{C_{\text{PCl}_3} \times C_{\text{Cl}_2}}{C_{\text{PCl}_5}} = \frac{\frac{a}{V} \cdot \frac{a}{V}}{\frac{1-a}{V}} = \frac{a^2}{(1-a)V}$$

Since the numbers of molecules of reactants and resultants are unequal, $K_P \neq K_C$. At any given temperature K_P remains constant, hence with increase of pressure P , a will diminish. That is, the extent of dissociation will decrease with pressure.

(d) *Synthesis of ammonia* : $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

This is a reaction in which the number of molecules of resultants is less than that of the reactants. Suppose we start with a mixture of N_2 and H_2 in 1 : 3 ratio in moles and let the extent of chemical transformation at equilibrium be x per mole of nitrogen. Then

	N_2	H_2	NH_3	Total
Initial moles	1	3	0	$= 4$
Moles at equilibrium	$1-x$	$3-3x$	$2x$	$= 4-2x$
Partial pressures	$\frac{1-x}{4-2x} P$	$\frac{3-3x}{4-2x} P$	$\frac{2x}{4-2x} P$	$= P$

$$\text{So, } K_P = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \cdot P_{\text{H}_2}^3} = \frac{\left[\frac{2x}{4-2x} P\right]^2}{\left[\frac{1-x}{4-2x} P\right] \left[\frac{3-3x}{4-2x} P\right]^3}$$

$$\text{or, } K_P = \frac{4x^2(4-2x)^2}{27(1-x)^4 P^2}$$

$$\text{If } x \text{ is small, } K_P = \frac{64}{27} \cdot \frac{x^2}{P^2}$$

It shows K_P which is constant at any given temperature, is determined by the ratio x/P . Further, with increase of P , x must also increase proportionately,

$$\text{for } P^2 = \frac{64}{27 K_P} \cdot x^2, \text{ i.e., } P = k'x$$

This means that with higher pressures, the yield of ammonia would be larger. This is a valuable information to the manufacturer of ammonia. We can also calculate K_C from this, by equation (IX.8),

$$\begin{aligned} K_C &= K_P (RT)^{-\Delta v} = \frac{64x^2}{27} \cdot \frac{1}{P^2} \cdot (RT)^{-(2-4)} \\ &= \frac{64x^2}{27} \cdot \left(\frac{RT}{P}\right)^2 \end{aligned}$$

$$\text{Since volume } V = (4-2x) \frac{RT}{P} \approx 4 \frac{RT}{P}, \text{ we have, } K_C = \frac{64x^2}{27} \cdot \left(\frac{V}{4}\right)^2 = \frac{4x^2 V^2}{27}.$$

(e) The dissociation of nitrogen tetroxide, $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$

So, we have, $K_P = P_{\text{NO}_2}^2 / P_{\text{N}_2\text{O}_4}$

If we start with 1 mole of N_2O_4 and α be the degree of dissociation, then at eqm., there are in all $(1+\alpha)$ gm-moles of gas, of which 2α gm-moles are NO_2 and $(1-\alpha)$ gm-moles N_2O_4 .

Hence
$$K_N = \frac{[2\alpha/(1+\alpha)]^2}{[(1-\alpha)/(1+\alpha)]} = \frac{4\alpha^2}{1-\alpha^2}$$

But
$$K_P = K_N \cdot P^{\Delta\nu} \quad (\text{from eqn. IX.9})$$

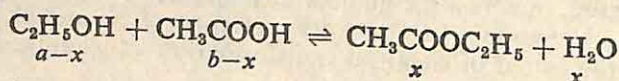
Since, $\Delta\nu = 1$,
$$K_P = \frac{4\alpha^2}{1-\alpha^2} P$$

' α ' can be easily obtained from vapour-density measurements and hence K_P is evaluated.

LIQUID SYSTEMS

The principle of the law of mass action is universally applicable to reactions in liquid systems and also in heterogeneous systems where components may occur in different phases. The esterification of acids is a classical example of equilibrium study in liquid systems.

(f) Esterification of acetic acid :



Let the total volume of the liquid system be V and let the initial amounts of alcohol and acid be a and b gm-moles and at equilibrium the amount of acid esterified be x . Then at equilibrium, the concentrations are.

$$C_{\text{alc}} = \frac{a-x}{V}, \quad C_{\text{acid}} = \frac{b-x}{V}, \quad C_{\text{ester}} = \frac{x}{V}, \quad C_{\text{H}_2\text{O}} = \frac{x}{V}$$

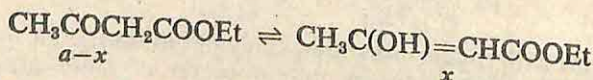
So,
$$K_C = \frac{C_{\text{ester}} \times C_{\text{H}_2\text{O}}}{C_{\text{alc}} \times C_{\text{acid}}} = \frac{x^2}{(a-x)(b-x)}$$

The equilibrium constant is therefore independent of the volume of the system. If we start with 1 mole of each, then

$$K_C = \frac{x^2}{(1-x)^2}, \quad \text{or} \quad x = \frac{2K_C \pm \sqrt{4K_C^2 - 4(K_C - 1)K_C}}{2(K_C - 1)}$$

Experimentally, at room temperature, $K_C = 4.0$. So, $x = 0.66$. It is obvious that with a given amount of acid and alcohol, we can calculate the expected yield of the ester at equilibrium.

(g) Keto-enol tautomerism :

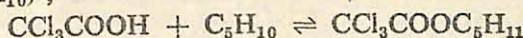


Obviously, the equilibrium between the two forms is governed by

$$K_C = \frac{C_{\text{enol}}}{C_{\text{keto}}} = \frac{x/V}{(a-x)/V} = \frac{x}{a-x}$$

The equilibrium constant of this reaction, and many others in solution, are affected markedly by the solvent, though the solvent would not participate directly. Thus, in this reaction, enolisation is only 0.5% in water but 46% in hexane solution

(h) Another equilibrium studied carefully in a liquid system is esterification with amylene (C_5H_{10});



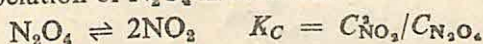
$$\text{Conc :} \quad \frac{a-x}{V} \quad \frac{b-x}{V} \quad \frac{x}{V}$$

If initial amounts of the acid and hydrocarbon be a and b moles in volume V and x moles be esterified, then

$$K = \frac{\frac{x}{V}}{\frac{a-x}{V} \cdot \frac{b-x}{V}} = \frac{xV}{(a-x)(b-x)}.$$

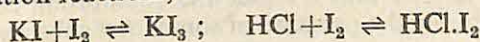
Of other examples of mass action study, which can be easily followed, we can mention

(i) the dissociation of N_2O_4 in solution.



Since NO_2 molecules are coloured and N_2O_4 molecules are colourless, the estimation can be done colorimetrically.

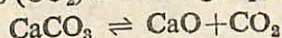
(ii) The iodination reactions, such as



are followed through measurements of distribution of iodine in two immiscible liquids (Sec. X.5).

HETEROGENEOUS SYSTEMS

(i) *Dissociation of calcium carbonate.* This is a heterogeneous chemical reaction, as one of the products (CO_2) is in the gas-phase while others are solids.



If, at a constant temperature, calcium carbonate is kept in a closed vessel, then the reaction proceeds with gradual increase in pressure of CO_2 until a constant pressure is obtained which we call dissociation pressure of calcium carbonate.

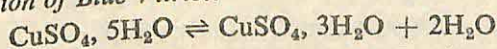
It is the generally accepted convention that the activities of solids should be regarded as unity. In the case of liquids, the standard state is the pure state (under 1 atm.), when activity is unity. But if it be present in liquid solution, as a first approximation, activity may be taken as equal to its mol-fraction.

Now, for dissociation of calcium carbonate, $a_{CaCO_3} = 1$, $a_{CaO} = 1$.

$$\therefore K_a = \frac{a_{CaO} \times a_{CO_2}}{a_{CaCO_3}} = a_{CO_2} \approx P_{CO_2}$$

assuming that carbon dioxide behaves ideally. Hence at any given temperature, the dissociation pressure of calcium carbonate would be a constant.

(j) *Dehydration of Blue Vitriol.*



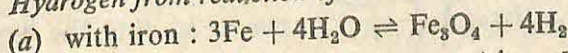
$$K_a = \frac{a_{CuSO_4 \cdot 3H_2O} \times a_{H_2O}^2}{a_{CuSO_4 \cdot 5H_2O}}$$

$$K_P = P_{H_2O}^2$$

So,

Hence, the vapour-pressure would reach a constant value.

(k) *Hydrogen from reduction of steam.*



$$\text{when} \quad K_a = \frac{a_{Fe_3O_4} \times a_{H_2}^4}{a_{Fe}^3 \times a_{H_2O}^4} = \left(\frac{a_{H_2}}{a_{H_2O}} \right)^4 \approx \left[\frac{P_{H_2}}{P_{H_2O}} \right]^4$$

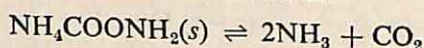
Thus the ratio of P_{H_2}/P_{H_2O} is constant, which has been substantiated from experiment. This means that with increase of steam-pressure higher yield of hydrogen is obtained.

(b) with carbon : $C + H_2O \approx CO + H_2$

where $K_a = \frac{a_{CO} \times a_{H_2}}{a_C \times a_{H_2O}} \approx \frac{P_{CO} \times P_{H_2}}{P_{H_2O}} = \frac{P_{H_2}^2}{P_{H_2O}}$ since $P_{CO} = P_{H_2}$

Hence, $K_P = \frac{P_{H_2}^2}{P_{H_2O}}$, i.e., $P_{H_2} \propto \sqrt{P_{H_2O}}$

(l) Dissociation of ammonium carbamate.



So, $K_a = \frac{a_{NH_3}^2 \times a_{CO_2}}{a_{solid}} \approx P_{NH_3}^2 \times P_{CO_2}$

Let P be the total pressure at equilibrium, then $P_{NH_3} = \frac{2}{3}P$ and $P_{CO_2} = \frac{1}{3}P$.

Hence, $K_P = \frac{4}{27}P^3$

IX.5. Influence of Inert Gases on the Equilibrium State of a Gaseous Reaction. It would be of interest to ascertain whether the equilibrium concentrations of the components would alter by the presence of some inert substances.

So long as temperature remains unaltered, K_P will not vary. We have

$$K_P = K_N (P)^{\Delta v}$$

Consider a reaction : $aA + bB + \dots \rightleftharpoons dD + eE + \dots$

Let the system contain $N_A, N_B, \dots, N_D, N_E, \dots$ mol-fractions of the components. Then

$$K_P = \frac{N_D^d \times N_E^e}{N_A^a \times N_B^b} (P)^{\Delta v}$$

Now

$$N_A = \frac{n_a}{n_0 + n_A + n_B + n_D + n_E} = \frac{n_a}{\Sigma n}$$

where n -terms are gm-molecules of the components, n_0 is the number of gm-molecules of the inert substance introduced. Thus we have,

$$K_P = \left[\frac{n_D^d \times n_E^e}{n_A^a \times n_B^b} \right] \left(\frac{P}{\Sigma n} \right)^{\Delta v} \dots (A)$$

Now, on the introduction of an inert gas in the system Σn will always increase. Several cases may arise :

(i) Addition of the inert gas at constant pressure :

(a) If $\Delta v = 0$, then $\left(\frac{P}{\Sigma n} \right)^{\Delta v} = 1$, hence the first factor in equation (A)

will not change, or the equilibrium remains undisturbed.

(b) If Δv is positive, then $\left(\frac{P}{\Sigma n} \right)^{\Delta v}$ diminishes and consequently the first factor will increase in magnitude. This is possible by increasing the concentrations of the resultants in the numerator and decreasing the concentrations of the reactants in the denominator. In other words, there would be more of reaction.

(c) If Δv is negative, then $\left(\frac{P}{\Sigma n} \right)^{\Delta v}$ increases, so that the first factor must decrease. In other words concentrations of the resultants would decrease. Hence the reaction will be depressed.

(ii) Addition of the inert gas at *constant volume* :

(a) when the inert gas is added to the system whose volume is kept constant, the total pressure P will increase proportionately with the number of moles of the inert gas added ; i.e., $\frac{P}{\sum n}$ will remain constant. Hence, the first factor in equation (A) will remain unchanged, or the equilibrium will not be disturbed in any reaction. Problem 8 in the next section will illustrate such an effect.

IX.6. Some Typical Numerical Examples.

Problem 1. Calculate the pressure in atmospheres necessary to obtain a 50% dissociation of PCl_5 at 250°C . The eqm. constant for the reaction, $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$, $K = 1.8$.

If we start with 1 mole of PCl_5 , the moles of different gases at eqm. are, $\text{PCl}_5 = 0.5$ moles, $\text{PCl}_3 = 0.5$ moles, $\text{Cl}_2 = 0.5$ moles. Total = 1.5 moles.

$$\text{The partial pressures are } P_{\text{PCl}_5} = P_{\text{PCl}_3} = P_{\text{Cl}_2} = \frac{0.5}{1.5}P$$

where P is the required total pressure in atmospheres.

$$\text{Hence } K_P = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{\left(\frac{0.5}{1.5}\right)^2 P^2}{\frac{0.5}{1.5}P} = \frac{1}{3}P$$

$$\text{or } \frac{1}{3}P = 1.8, \text{ i.e., } P = 5.4 \text{ atmospheres.}$$

This shows that in a reaction of the type $AB \rightarrow A+B$, the total pressure required for 50% dissociation is numerically 3 times K_P .

Problem 2. At 25°C , 1 mole of acetic acid and 1 mole of ethanol are mixed. At eqm. 0.667 moles of acid have reacted. Calculate K_C . How much ester would be obtained if 2 moles of acid were taken with 1 mole ethanol under the same conditions?

$$K_C = \frac{C_{\text{ester}} \times C_{\text{H}_2\text{O}}}{C_{\text{acid}} \times C_{\text{alcohol}}} = \frac{(0.667/V)(0.667/V)}{(0.333/V)(0.333/V)} = 4.00$$

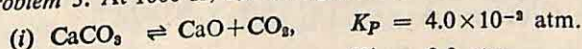
In the other experiment, let x moles of acid be transformed, then

$$\begin{array}{ccccccc} \text{CH}_3\text{COOH} & + & \text{EtOH} & \rightleftharpoons & \text{CH}_3\text{COOEt} & + & \text{H}_2\text{O} \\ \text{Conc :} & & (2-x)/V & & x/V & & x/V \\ & & x^2 & & x^2 & & \\ \therefore & & K_C = 4 = \frac{x^2}{(2-x)(1-x)} & & = \frac{x^2}{2-3x+x^2} \end{array}$$

whence $x = 3.15$ or 0.85 .

Since the first solution is absurd, amount of ester at eqm. is 0.85 moles.

Problem 3. At 1000°K , for the equilibria,



Solid carbon, CaO and CaCO_3 are mixed and allowed to attain eqm. at 1000°K . What is the pressure of CO ?

$$K_P = \frac{a_{\text{CaO}} \times a_{\text{CO}_2}}{a_{\text{CaCO}_3}} \approx P_{\text{CO}_2}; \quad K'_P = \frac{a_{\text{CO}}^2}{a_{\text{C}} \cdot a_{\text{CO}_2}} \approx \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}}$$

$$\therefore K_P \cdot K'_P = P_{\text{CO}}^2 \text{ or } P_{\text{CO}} = \sqrt{K_P \cdot K'_P} = \sqrt{4 \times 10^{-2} \times 2.0} = 0.28 \text{ atmospheres.}$$

Problem 4. At 1000°C , the pressure of iodine gas is found to be 0.112 atm. whereas the expected pressure is 0.074 atm. The increased pressure is due to dissociation ; $\text{I}_2 \rightleftharpoons 2\text{I}$. Calculate K_P . Also find out the pressure at which I_2 will be 90% dissociated at 1000°C .

$$\begin{array}{ccccccc} \text{I}_2 & \rightleftharpoons & 2\text{I} & \text{Total} & & & \\ 1-a & & 2a & 1+a; & & & \alpha = \text{degree of dissociation.} \end{array}$$

Since pressure is proportional to number of moles of entities of gases ; $P/P_0 = 1+\alpha$, where P = observed pressure, P_0 = calculated pressure (having no dissociation).

$$\therefore \alpha = \frac{P-P_0}{P_0}$$

Now

$$P_I = \frac{2\alpha}{1+\alpha} P; \quad P_{I_2} = \frac{1-\alpha}{1+\alpha} P$$

Hence

$$K_P = \frac{\left[\frac{2\alpha}{1+\alpha} P \right]^2}{\left(\frac{1-\alpha}{1+\alpha} P \right)} = \frac{4\alpha^2}{1-\alpha^2} P = \frac{4 \left(\frac{P-P_0}{P_0} \right)^2}{1 - \left(\frac{P-P_0}{P_0} \right)^2} P$$

$$= \frac{4(P-P_0)^2}{2P_0-P} = \frac{4(0.038)^2}{0.036} = 15.2 \times 10^{-2}$$

When degree of dissociation $\alpha = 0.90$, we have

$$P = K_P \frac{(1-\alpha^2)}{4\alpha^2} = 15.2 \times 10^{-2} \times \frac{(1-0.81)}{4 \times 0.81} = 8.9 \times 10^{-2} \text{ atm.}$$

Problem 5. The ammonia in eqm. with a 1 : 3 N_2 - H_2 mixture at 20 atmospheres and 427°C amounts to 16%. Calculate K_P and K_C for



For 100 moles of mixture, there are 16 moles of ammonia. Hence, every mole of mixture contains 0.16 moles NH_3 , 0.21 moles N_2 and 0.63 moles H_2 . Their partial pressures are

$$P_{NH_3} = \frac{0.16}{1} \times 20 = 3.2 \text{ atm}; \quad P_{H_2} = \frac{0.63}{1} \times 20 = 12.6 \text{ atm}; \quad P_{N_2} = \frac{0.21}{1} \times 20 = 4.2 \text{ atm.}$$

 $\therefore$

$$K_P = \frac{P_{NH_3}}{P_{H_2}^{3/2} \times P_{N_2}^{1/2}} = \frac{3.2}{(12.6)^{3/2} \times (4.2)^{1/2}} = 3.49 \times 10^{-2}$$

and

$$K_C = K_P(RT)^{-\Delta v} = K_P(RT)^{-1} = \frac{3.49 \times 10^{-2}}{(0.082 \times 700)} = 6.1 \times 10^{-4}$$

Problem 6. Ammonia in eqm. with 1 : 3 N_2 - H_2 mixture at 44 atm and 350°C is 15% by weight. Calculate K_P .

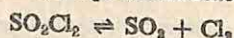


100 gms mixture contains 15 gms ammonia, $\frac{14 \times 85}{17}$ gms N_2 and $\frac{3 \times 85}{17}$ gms of H_2 . Then,

	NH_3	N_2	H_2	Total
in moles	0.88	2.5	7.5	10.88
in pressures	$\frac{0.88 \times 44}{10.88}$	$\frac{2.5 \times 44}{10.88}$	$\frac{7.5 \times 44}{10.88}$	44

$$\therefore K_P = \frac{[0.88 \times 44 / 10.88]}{[2.5 \times 44 / 10.88]^{1/2} [7.5 \times 44 / 10.88]^{3/2}} = 6.7 \times 10^{-2}$$

Problem 7. At 127°C , the eqm. constant K_P for the reaction



is 2.4 in atmospheres. 6.75 gms of SO_2Cl_2 are placed in an empty 1-litre bulb and the temperature raised to 127°C . What would be the pressure of SO_2 , Cl_2 and SO_2Cl_2 gases?

Also calculate the pressure of these gases if the same quantity of SO_2Cl_2 were taken into the bulb already containing chlorine at 1 atm. Compare if the results are consistent with the Le-Chatelier principle.

In absence of dissociation, the initial pressure (P) of SO_2Cl_2 is

$$P \times 1 = \frac{6.75}{135} \times 0.082 \times (273 + 127) \quad \text{or} \quad P = 1.64 \text{ atm.}$$

Now

$$K_P = \frac{P_{SO_2} \times P_{Cl_2}}{P_{SO_2Cl_2}} = \frac{P_{SO_2}^2}{P - P_{SO_2}} \quad [\text{since } P_{SO_2} = P_{Cl_2}]$$

 $\therefore$

$$\frac{P_{SO_2}^2}{P - P_{SO_2}} = \frac{P_{SO_2}^2}{1.64 - P_{SO_2}} = 2.4$$

$$\text{Solving : } P_{SO_2} = P_{Cl_2} = 1.118 \text{ atm, } P_{SO_2Cl_2} = 0.522$$

(b) When the bulb already contains chlorine at 1 atm, let the partial pressure of SO_2 at eqm. be π . Then $P_{\text{Cl}_2} = (\pi + 1)$ and $P_{\text{SO}_2\text{Cl}_2} = 1.64 - \pi$

$$\therefore K_P = \frac{\pi(\pi+1)}{1.64-\pi} = 2.4$$

Solving : $\pi = 0.912$, i.e., $P_{\text{SO}_2} = 0.912$; $P_{\text{Cl}_2} = 1.912$; $P_{\text{SO}_2\text{Cl}_2} = 0.728$.

The addition of chlorine has diminished the extent of dissociation of SO_2Cl_2 . This is expected from Le-Chatelier principle, which predicts the removal of chlorine, obviously by the reverse process.

Problem 8. (a) In phosgene gas reaction at 400°C , the initial pressures are $P_{\text{CO}} = 342$ mm and $P_{\text{Cl}_2} = 352$ mm. and the total pressure at eqm. is 440 mm. $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$.

Calculate the percentage dissociation of phosgene at 400°C at 1 atmosphere.

(b) What will be the extent of dissociation if N_2 is present in the system with a pressure of 0.4 atm., the total pressure being the same 1 atmosphere.

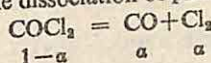
(a) Let x be the partial pressure of phosgene gas at eqm. At eqm. then,

$$P_{\text{CO}} = (342-x) \text{ mm}, P_{\text{Cl}_2} = (352-x) \text{ mm}, P_{\text{COCl}_2} = x \text{ mm}.$$

$$\therefore (352-x) + (342-x) + x = 440, \text{ i.e., } x = 254 \text{ mm} = 0.334 \text{ atm.}$$

$$\therefore P_{\text{CO}} = 342 - 254 = 88 \text{ mm} = 0.116 \text{ atm.}, P_{\text{Cl}_2} = 352 - 254 = 98 \text{ mm} = 0.128 \text{ atm.}$$

The eqm. constant for the dissociation of phosgene ;



$$1-\alpha \quad \alpha \quad \alpha$$

$$\therefore K_P = \frac{P_{\text{CO}} \times P_{\text{Cl}_2}}{P_{\text{COCl}_2}} = \frac{0.116 \times 0.128}{0.334} = 4.4 \times 10^{-2}$$

$$\text{But } K_P = \frac{\alpha^2 P}{1-\alpha^2} = 4.4 \times 10^{-2},$$

Since $P = 1$, $\alpha = 0.206$, i.e., dissociation is 20.6%.

(b) When inert N_2 is present with $P_{\text{N}_2} = 0.4$ atm, the total pressure of the reactants and resultants at eqm. = 0.6 atm.

$$\text{Hence } K_P = \frac{\alpha_1^2 P}{1-\alpha_1^2}, \text{ where } \alpha_1 \text{ is the degree of dissociation in presence of } \text{N}_2.$$

$$\text{or } \frac{\alpha_1^2 (0.6)}{1-\alpha_1^2} = 4.4 \times 10^{-2}, \text{ whence } \alpha_1 = 0.26, \text{ i.e., } 26\%.$$

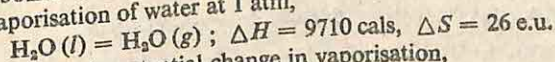
The presence of N_2 has enhanced the extent of dissociation.

IX.7. The Thermodynamic Criterion for Equilibrium. The basic criterion for equilibrium of any system, physical or chemical, is that the thermodynamic potential of the system must be minimum. In other words, at equilibrium the thermodynamic potential change ΔG must be zero, i.e., $\Delta G_{P,T} = 0$. [See, Sec. IV.40]. More explicitly, when

$$\begin{array}{ll} \Delta G_{P,T} = 0, & \text{the system is at equilibrium,} \\ \Delta G_{P,T} = -ve, & \text{the process would tend to proceed spontaneously,} \\ \Delta G_{P,T} = +ve, & \text{the process would tend to move in the opposite direction.} \end{array}$$

The calculation of ΔG of a system in a specified state will indicate whether a given process would be spontaneous or if the equilibrium has been attained. If $\Delta G = 0$, the initial and final states can exist at equilibrium with each other, with no change. If ΔG be negative, the process will be spontaneous. We may illustrate with some examples.

(i) In the vaporisation of water at 1 atm,



So, the thermodynamic potential change in vaporisation,

$$\Delta G = \Delta H - T\Delta S = 9710 - 26T.$$

$$(a) \text{ If } \Delta G = 0, T = \frac{9710}{26} = 373.4^\circ\text{K}$$

i.e., equilibrium will be attained between liquid and vapour at 373.4°K (100°C) at 1 atm, which is an observed fact.

(b) If $T = 400^\circ\text{K}$, $\Delta G = 9710 - 400 \times 26 = -690$ cal. The negative value of ΔG indicates that at this temperature vaporisation would spontaneously occur—an experimental fact.

(ii) In the formation of water at 25°C and 1 atm,



The entropy change of the formation of H_2O ;

$$\Delta S = S_{\text{H}_2\text{O}(l)} - S_{\text{H}_2} - \frac{1}{2}S_{\text{O}_2} = -39 \text{ e.u.}$$

$\therefore$ The thermodynamic potential change in the formation of $\text{H}_2\text{O}(l)$ is

$$\Delta G = \Delta H - T\Delta S = -68320 - (298)(-39) = -56698 \text{ cal.}$$

Since ΔG is negative, it is thermodynamically predicted that formation of water would proceed spontaneously. But a mixture of H_2 and O_2 does not seem to react appreciably at 25°C . This is only because of the extreme slow rate of the reaction, which is not a concern of thermodynamics. If the rate be accelerated by a catalyst or a spark, the equilibrium will be established and it will be much towards the direction of water.

(iii) In the oxidation of ethyl alcohol to acetic acid at 250°C and 1 atm,



$$\Delta G: \quad \begin{array}{cccc} & -41770 & 0 & -93800 & -68320 \end{array}$$

Hence the net thermodynamic potential change of the process,

$$\Delta G = -93800 - 68320 - (-41770) = -120350 \text{ cal.}$$

This highly negative thermodynamic potential change of the process predicts spontaneous oxidation of alcohol. Hence, if a suitable way (a catalyst) is found, the oxidation will readily occur.

IX.8. Equilibrium Constant and Thermodynamic Potential Change: The Reaction Isotherm. It is easy to find a correlation between the thermodynamic potential change and the eqm. constant of a chemical process.

Consider a general reaction, $aA + bB \rightleftharpoons dD + eE$

in which suppose at a given temperature T and at a given set of arbitrarily chosen concentrations (or pressures), a moles of A react with b moles of B yielding d moles of D and e moles of E .

The change in the thermodynamic potential in the system due to the chemical reaction at constant temperature and pressure, would be,

$$\Delta G = G_{\text{resultants}} - G_{\text{reactants}} = d\mu_D + e\mu_E - a\mu_A - b\mu_B$$

where μ -terms are the respective chemical potentials.

Since $\mu = RT \ln a + z$ (equation IV.117), we have

$$\Delta G = d[RT \ln a_D + z_D] + e[RT \ln a_E + z_E] - a[RT \ln a_A + z_A] - b[RT \ln a_B + z_B]$$

$$= RT \ln \frac{a_D^d \times a_E^e}{a_A^a \times a_B^b} + dz_D + ez_E - az_A - bz_B$$

$$= RT \ln \frac{a_D^d \times a_E^e}{a_A^a \times a_B^b} + Z \text{ (constant)}$$

where $a_A, a_B \dots$ etc. are the activities of the components in the arbitrarily chosen conditions for the reaction.

It would be remembered that this relation is valid for any chosen state and therefore would also be valid if we start with the components in the equilibrium state. Then, using suffix ϵ for denoting equilibrium conditions,

$$\Delta G^\epsilon = RT \ln \frac{a_{\epsilon D}^d \times a_{\epsilon E}^e}{a_{\epsilon A}^a \times a_{\epsilon B}^b} + Z = RT \ln K_a + Z$$

But at equilibrium, $\Delta G^\epsilon = 0$, hence $Z = -RT \ln K_a$

Then for any chemical reaction, the thermodynamic potential change,

$$\begin{aligned} \Delta G &= -RT \ln K_a + RT \ln \frac{a_D^d \times a_E^e}{a_A^a \times a_B^b} \\ &= -RT \ln K_a + RT \sum \nu \ln a \end{aligned}$$

This relation is commonly known as the *reaction isotherm*. ... (IX.10)

When the systems approach ideality, activities may be replaced by fugacities or pressures or by concentrations. The modified forms of the reaction isotherm would be

$$\left. \begin{aligned} \Delta G_C &= -RT \ln K_C + RT \sum \nu \ln C \\ \Delta G_P &= -RT \ln K_P + RT \sum \nu \ln P \end{aligned} \right\} \dots \text{(IX.11)}$$

The standard states chosen in each case must be specified.

The importance of the isotherm lies in the fact that it can predict in which way a reaction, in a given set of conditions, would proceed. In eqn. (IX.11), if the arbitrarily chosen concentrations $\sum \nu \ln C$ is less than $\ln K_C$, ΔG is $-ve$, a spontaneous reaction would take place. If $\sum \nu \ln C$ be greater than $\ln K_C$, the reaction will not occur. In that case if we reduce the concentrations of resultants and increase those of reactants, the possibility of reaction in the desired direction would improve. It is thus that thermodynamics provides us the clue to the knowledge of conditions favouring a chemical process.

Again,
$$\Delta G = -RT \ln K_a + RT \sum \nu \ln a$$

If the chemical change be carried out in such conditions that every reactant and resultant be maintained at unit activities, i.e., all the reactants and resultants are in standard states, then $\sum \nu \ln a = 0$, and so,

$$\Delta G^0 = -RT \ln K_a \dots \text{(IX.11a)}$$

ΔG^0 is the *standard thermodynamic potential change*, accompanying conversion of reactants in standard states to resultants in their standard states.

This shows that eqm. constant is a measure of the standard thermodynamic potential change of the process. Experimental determination of ΔG , for which there are several methods, will thus enable us to evaluate K_P and *vice versa*.

We can now rewrite equation (IX.10) as

$$\Delta G = \Delta G^0 + RT \sum \nu \ln a \dots \text{(IX.12)}$$

As before, in ideally behaving systems we have

$$\left. \begin{aligned} \Delta G^0 &= -RT \ln K_C \text{ and } \Delta G = \Delta G^0 + RT \sum \nu \ln C \\ \Delta G^0 &= -RT \ln K_P \text{ and } \Delta G = \Delta G^0 + RT \sum \nu \ln P \end{aligned} \right\} \dots \text{(IX.13)}$$

These relations (IX.11) and (IX.13) are of unique importance to the chemist.

Problem 9. At 1000°K , the value of K_P for the reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$, is 3.5. What would be the thermodynamic potential change if 2 moles of SO_3 at 1 atm are formed from SO_2 at 0.1 atm and O_2 at 0.2 atm at this temperature? [Use R in litre-atm.]

$$\begin{aligned} \Delta G &= -RT \ln K_P + RT \ln \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} \\ &= -RT \ln 3.5 + RT \ln \frac{(1)^2}{(0.1)^2 \times (0.2)} = 9890 \text{ cal.} \end{aligned}$$

Since
$$\Delta G^0 = -RT \ln K$$

we may write ;
$$K = e^{\frac{-\Delta G^0}{RT}} = 10^{\frac{-\Delta G^0}{2.3RT}} = 10^{\frac{\Delta S_0}{2.3R}} \cdot 10^{\frac{-\Delta H^0}{2.3RT}} \dots \text{(IX.14)}$$

since
$$\Delta G^0 = \Delta H^0 - T\Delta S_0 \text{ (eqn. IV.53).}$$

It is evident that

- When $\Delta G < 0$, K will be greater than unity and will increase as ΔG^0 becomes more and more negative ;
- the more negative the value of ΔH^0 , the larger will be the value of eqm. constant K ;
- the larger the value of ΔS_0 , the higher will be the magnitude of K .

The higher values of K indicate greater extent of reaction to produce the resultants. That is, the reaction will be favoured when ΔG^0 and ΔH^0 are very negative and

Le Chatelier principle gives a qualitative idea as to the direction in which equilibrium will be shifted when temperature is changed. It is possible to deduce a quantitative expression for the variation of eqm. constant with temperature from thermodynamic considerations.

The reaction isotherm : $\Delta G = -RT \ln K_P + RT \sum \nu \ln P$

Differentiating with respect to temperature at constant pressure,

$$\frac{\partial(\Delta G)}{\partial T} = -RT \frac{\partial \ln K_P}{\partial T} - R \ln K_P + RT \frac{\partial \sum \nu \ln P}{\partial T} + R \sum \nu \ln P$$

The term $\sum \nu \ln P$ is a fixed quantity containing arbitrarily chosen pressures of the components, hence $\frac{\partial \sum \nu \ln P}{\partial T} = 0$. Multiplying both sides by T ,

$$\begin{aligned} T \frac{\partial(\Delta G)}{\partial T} &= -RT^2 \frac{\partial \ln K_P}{\partial T} - RT \ln K_P + RT \sum \nu \ln P \\ &= -RT^2 \frac{\partial \ln K_P}{\partial T} + \Delta G \end{aligned}$$

$$\text{Hence, } RT^2 \frac{\partial \ln K_P}{\partial T} = \Delta G - T \frac{\partial(\Delta G)}{\partial T} \quad \dots (IX.15)$$

But from Gibbs-Helmholtz equation, $\Delta G - T \frac{\partial(\Delta G)}{\partial T} = \Delta H_T$

where ΔH_T is the heat-change (*i.e.*, heat of reaction) at temperature T .

$$\therefore RT^2 \frac{\partial \ln K_P}{\partial T} = \Delta H_T$$

$$\therefore \frac{\partial \ln K_P}{\partial T} = \frac{\Delta H}{RT^2} \quad \dots (IX.16)$$

This is commonly known as the *van't Hoff equation*, which gives the variation of K_P with temperature T .

We know further $K_P = K_C (RT)^{\Delta \nu}$

or, $\ln K_P = \ln K_C + \Delta \nu \ln R + \Delta \nu \ln T$

or $\frac{\partial \ln K_P}{\partial T} = \frac{\partial \ln K_C}{\partial T} + \frac{\Delta \nu}{T}$

Substituting this in the equation above (at const. pressure),

$$\frac{\partial \ln K_C}{\partial T} = \frac{\Delta H_T}{RT^2} - \frac{\Delta \nu}{T} = \frac{\Delta H_T - \Delta \nu RT}{RT^2} = \frac{\Delta H_T - P \Delta \nu}{RT^2}$$

$$\text{or } \frac{\partial \ln K_C}{\partial T} = \frac{\Delta U_T}{RT^2} \quad \dots (IX.17)$$

where ΔU is the energy-change at constant volume, *i.e.*, heat-change at constant volume. This relation for the variation of equilibrium constant K_C with temperature at constant volume is often mentioned as *van't Hoff isochore*.

IX.11. The Integration of the van't Hoff Equation. The integration of the van't Hoff equation (IX.16) would enable us to calculate numerically the shift of the equilibrium-constant with temperature.

$$\text{Now, } \int d \ln K_P = \frac{\Delta H}{R} \int \frac{dT}{T^2} \quad (\text{assuming } \Delta H \text{ as constant})$$

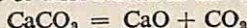
or
$$\ln K_P = -\frac{\Delta H}{R} \cdot \frac{1}{T} + C' \text{ (constant)}$$

Integrating between two temperatures, T_1 and T_2 , such that $T_1 > T_2$, we have,

$$\ln \frac{K_{P_1}}{K_{P_2}} = -\frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \frac{\Delta H}{R} \left[\frac{T_1 - T_2}{T_1 T_2} \right] \quad \dots \text{(IX.18)}$$

If the reaction be exothermic, i.e., ΔH is $-ve$, then the expression on the right-hand is negative, hence $K_{P_1} < K_{P_2}$. It means that with rise of temperature, K_P will diminish, i.e., resultants (at equilibrium) would be less. In other words, exothermic reactions are not favoured by rise of temperatures. If the reaction be endothermic, $K_{P_1} > K_{P_2}$, i.e., endothermic reactions would be favoured by rise in temperature. These are exactly the results expected from Le Chatelier and Braun principle.

Problem 15. The dissociation constant of CaCO_3 at 900°C and 1000°C are 790 mm and 2940 mm. Calculate the heat of dissociation at this temperature-range.



$$K_a = \frac{a_{\text{CaO}} \times a_{\text{CO}_2}}{a_{\text{CaCO}_3}} = a_{\text{CO}_2}, \text{ hence } K_P = P_{\text{CO}_2} = P \text{ (say)}$$

Then
$$\ln \frac{K_P}{K_{P'}} = \ln \frac{P}{P'} = -\frac{\Delta H}{R} \left[\frac{1}{T} - \frac{1}{T'} \right];$$

i.e.,
$$\ln \frac{790}{2940} = -\frac{\Delta H}{2} \left[\frac{1}{1173} - \frac{1}{1273} \right] \text{ or } \Delta H = 39646 \text{ cal.}$$

Since,
$$\ln K_P = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \text{constant}$$

or
$$\log K_P = -\frac{\Delta H}{2.3 R} \cdot \frac{1}{T} + \text{constant} \quad \dots \text{(IX.19)}$$

A plot of $\log K_P$ against $\frac{1}{T}$ would be linear, and the slope of the curve will give the value of ΔH , as illustrated in Fig. IX.1.

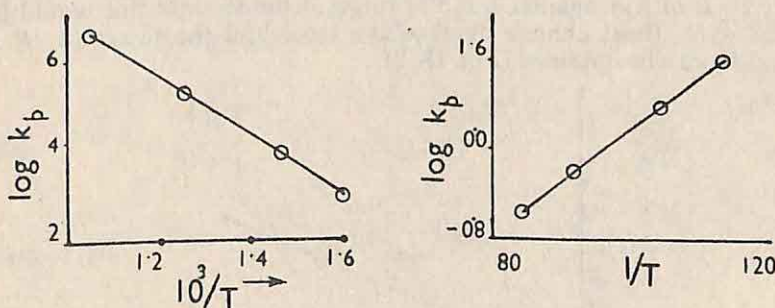
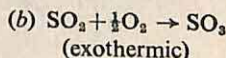
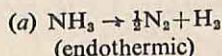


FIG. IX.1



If ΔH , the heat of reaction, be very small, i.e., $\Delta H \rightarrow 0$, as in the reaction between ethyl alcohol and acetic acid, $\ln K = \text{constant}$, i.e., eqm. constant does not change with temperature.

The relation (IX.18) is only an approximate one as ΔH has been assumed constant. It is known that ΔH often varies considerably with temperature. A proper integration of the van't Hoff equation may now be attempted.

Consider the reaction, $aA + bB \rightleftharpoons dD + eE$

Now from Kirchhoff's equation, we know,

$$\frac{\partial(\Delta H)}{\partial T} = \Delta C_P = C_{P_{\text{resultant}}} - C_{P_{\text{reactant}}}$$

$$\text{or} \quad \Delta H_T - \Delta H_0 = \alpha T + \frac{\beta T^2}{2} + \frac{\gamma T^3}{3} + \dots \quad \dots \text{ (IV.28)}$$

where ΔH_T and ΔH_0 are the heat-changes at $T^\circ\text{K}$ and 0°K respectively.

The van't Hoff equation will then be

$$\frac{\partial \ln K_P}{\partial T} = \frac{\Delta H_T}{RT^2} = \frac{\Delta H_0}{RT^2} + \frac{\alpha}{RT} + \frac{\beta}{2R} + \frac{\gamma T}{3R} + \dots$$

$$\text{or} \quad \ln K_P = -\frac{\Delta H_0}{RT} + \frac{\alpha}{R} \ln T + \frac{\beta T}{2R} + \frac{\gamma T^2}{6R} + \dots I \quad \dots \text{ (IX.20)}$$

where I is the integration constant of the isochore.

This is the proper integrated form of the van't Hoff equation. There is no way of direct measurement of the integration constant I . As such the evaluation of K_P from this relation proves difficult.

The constants $\alpha, \beta, \gamma, \dots$ etc. are available from direct measurements of heat-capacities of the reactants and resultants at different temperatures. If ΔH_T , the heat of reaction, is also determined at different temperatures, we can find ΔH_0 with the help of equation (IV.28). Thus, thermal measurements give us the constants on the right-hand side of equation (IX.20) except ' I '.

In those cases, when K_P can be experimentally determined, the value of I will be at once available from this equation.

Rewriting equation (IX.20),

$$R \ln K_P = -\frac{\Delta H_0}{T} + \alpha \ln T + \frac{\beta}{2} T + \frac{\gamma}{6} T^2 \dots + IR = -\frac{\Delta H_0}{T} + A + IR$$

where $A = \alpha \ln T + \frac{\beta}{2} T + \frac{\gamma}{6} T^2 + \dots$ such that ' A ' is a function of temperature only for any given reaction.

$$\text{That is,} \quad A - R \ln K_P = \frac{\Delta H_0}{T} - IR \quad \dots \text{ (IX.21)}$$

If we plot $(A - R \ln K_P)$ against $1/T$, the slope of the straight line would lead to the value of ΔH_0 (heat change at absolute zero) and the intercept IR . Thus, both I and ΔH_0 can be obtained (Fig. IX.2).

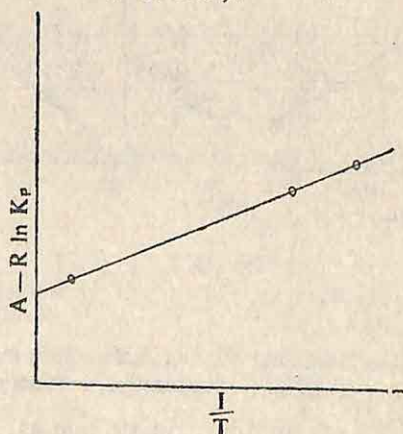


FIG. IX.2 Determination of I and ΔH_0

Problem 15. Given $C_{P_{H_2}} = 6.5 + 0.0009T$; $C_{P_{Br_2}} = 7.4 + 0.001T$, $C_{P_{HBr}} = 6.5 + 0.001T$.

Write down an expression for ΔG° for the reaction, $\frac{1}{2}H_2 + \frac{1}{2}Br_2 = HBr$, in which $\log K_P = 2.44$ at 1381°K , and $\Delta H_0 = -11970$ cal.

Now, $\Delta C_P = C_{P_{HBr}} - \frac{1}{2}C_{P_{H_2}} - \frac{1}{2}C_{P_{Br_2}} = -0.45 + 0.00005T$

Since
Again

$$\Delta C_P = \alpha + \beta T, \quad \text{we have } \alpha = -0.45, \beta = +0.00005$$

$$\log K_P = 2.44, \quad \text{i.e., } \ln K_P = 5.62$$

And

$$\ln K_P = \frac{-\Delta H_0}{RT} + \frac{\alpha}{R} \ln T + \frac{\beta}{2R} T + I \quad (\text{see equation IX.20})$$

or

$$5.62 = \frac{11970}{2 \times 1381} + \frac{(-.45)}{2} \times 2.303 \log 1381 + \frac{0.00005}{4} \times 1381 + I,$$

whence

$$I = 2.9$$

$\therefore$

$$\Delta G^\circ = -RT \ln K_P = \Delta H_0 - \alpha T \ln T - \frac{\beta}{2} T^2 - IRT$$

$$= -11970 + 0.45T \ln T - 0.000025 T^2 - 5.8T$$

IX.12. Calculation of Eqm. Constant K_P of a Gaseous Reaction (Theoretical). It is possible to employ the basic thermodynamic relations to evaluate the eqm. constant of a gaseous chemical change.

For a solid subliming into a gas, we have two thermodynamic relations :

$$(i) \text{ Clausius-Clapeyron equation, } \frac{\partial \ln P}{\partial T} = \frac{L_S}{RT^2} \quad \dots (I)$$

$$(ii) \text{ Kirchhoff's equation, } \frac{\partial L_S}{\partial T} = C_{P_g} - C_{P_s} = \Delta C'_P \quad \dots (II)$$

where L_S = molar latent heat of sublimation.

$$\text{From (II),} \quad L_S = L_{S_0} + \int_0^T \Delta C'_P dT \quad \dots (III)$$

$$\text{From (I) and (III), } \frac{\partial \ln P}{\partial T} = \frac{L_{S_0} + \int_0^T \Delta C'_P dT}{RT^2}$$

$$\text{or} \quad \ln P = -\frac{L_{S_0}}{RT} + \int_0^T \frac{\Delta C'_P dT}{RT^2} + i \quad \dots (IV)$$

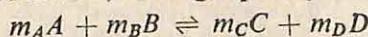
where i = chemical constant (see Sec. IV.47).

$$\text{But} \quad \int_0^T \frac{\Delta C'_P dT}{RT^2} = -\int_0^T \frac{\Delta C'_P dT}{RT} + \int_0^T \frac{\Delta C'_P}{RT} dT$$

$$\text{(from III),} \quad = \frac{L_{S_0} - L_S}{RT} + \int_0^T \frac{\Delta C'_P}{RT} dT, \quad \dots (V)$$

$$\therefore \text{ From (IV),} \quad \ln P = -\frac{L_S}{RT} + \int_0^T \frac{\Delta C'_P dT}{RT} + i \quad \dots (VI)$$

Now, consider a chemical reaction, in the gas phase,



$$\text{We have,} \quad K_P = \frac{P_C^{m_C} \times P_D^{m_D}}{P_A^{m_A} \times P_B^{m_B}}, \quad (P\text{-terms are partial pressures})$$

$$\text{and} \quad \frac{d \ln K_P}{dT} = \frac{\Delta H^G}{RT^2}$$

The superscript G will be used for gaseous state and S for solid state. ΔH^G is thus the heat of reaction in the gaseous state.

tions of the constituents when eqm. is reached. The task becomes comparatively easy when we can measure some physical property such as vapour-density, refractive index, optical rotation, electrical conductance, etc.

In simple gaseous dissociation such as $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, or $\text{COCl}_2 \rightleftharpoons \text{CO} + \text{Cl}_2$ etc, the density changes and becomes constant when eqm. is reached. The variation in density is measured at constant volume [by actually measuring pressures in a constant volume Victor Meyer's apparatus]. The density measurements give the value of α , the degree of dissociation and hence K_p . The method is applicable only in cases where dissociation is accompanied with change in number of moles.

In the determination of equilibrium in hydrolysis or in mutarotation of sugar, usually the polarimetric measurement of optical rotation is taken advantage of. In ionic equilibria, such as the dissociation of organic acids, the conductance measurement of solutions is used to ascertain the dissociation constant.

But, more frequently, method of chemical analysis is required and adequate precaution is needed to carry out the analysis very quickly so that the eqm. may not alter on removal of a reactant or a product from the system. The shift of eqm. is often prevented by sudden "chilling" of the system after attainment of eqm. or removal of catalyst, or addition of a chemical reagent in large excess. Such steps help in preservation of the equilibrium by reducing the rates of reaction practically to nil.

In hydrolysis of esters, *e.g.*, $\text{CH}_3\text{COOEt} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{EtOH}$, an aliquot part from the equilibrium mixture is taken out and immediately added to a large volume of water. The concentration thus becomes too low for undergoing change in a measurable rate and the eqm. is maintained. The dilute solution is next titrated against standard alkali to ascertain the amount of acid formed. The extent of hydrolysis, and hence the eqm. constant K_c , can then be easily calculated.

In the equilibrium, $\text{KI} + \text{I}_2 \rightleftharpoons \text{KI}_3$, the eqm. concentrations are obtained from a study of the partition coefficients of iodine distributed between two immiscible solvents [Sec. X.5] in presence and in absence of KI. Partition coefficient measurements are used also in some other reactions.

The chemical methods used for studying gaseous equilibria are classified as either static or dynamic. The classic example of static method is the study of eqm. $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ by Bodenstein. Small glass bulbs of known volume were filled with hydrogen iodide at different pressures at room temperature and sealed off. The bulbs were then kept in constant high temperature baths for considerable time till eqm. is reached. The bulbs were then taken out and quickly cooled to a very low temperature so as to freeze the eqm. inside. The bulbs were then opened inside caustic alkali solution and the hydrogen is collected in a eudiometer tube and the volume measured. HI and I_2 are absorbed in the alkali. The amount of

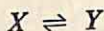
hydrogen gives the extent of dissociation (α) from which $K_p = \frac{4\alpha^2}{(1-\alpha)^2}$ is known.

In another set of experiments, bulbs were filled with known mixtures of hydrogen and iodine and the unreacted hydrogen measured at eqm. as before. The eqm. constant for dissociation was found to be same.

The dynamic method in the study of equilibria had been particularly followed by Haber and Nernst. Subsequently other workers, like Larson and Dodge, improved the technique. The principle is to run the mixture of reactant gases through a hot tube containing a suitable catalyst. This assures quick attainment of eqm., as in the case of N_2 and H_2 in ammonia synthesis. The outgoing gases are rapidly "chilled" to a much lower temperature where reaction-rate is negligible. The products are then analysed. Whether eqm. had been attained in the hot tube can be tested by flowing the reaction mixture at successively slower rates until there is no longer any change in the extent of reaction.

IX.14. Equilibrium Constant from Partition Functions. We have seen how the equilibrium constant can be derived by considering the thermodynamic potentials of the reactants and the resultants. In Chapter VII, we have noticed that the

thermodynamic potentials and free energies can be determined from the molecular properties. We may therefore attempt now a molecular interpretation of the equilibria. To illustrate we may start with a simple gaseous equilibrium between two isomers,



It would be first necessary to know the energy-levels of both the types of isomeric molecules. Suppose the energy-states of X and of Y be represented as in Fig. IX.3 ; the energy levels of X are $0, \epsilon_x, 2\epsilon_x, 3\epsilon_x \dots$ etc. and of Y are $0, \epsilon_y, 2\epsilon_y, 3\epsilon_y \dots$ etc. The spacing of energy levels are different for the two species, and the ground-state or zero-point energy-levels of the two isomeric types are also different. The difference of the molar ground-state energies may be denoted by ΔE_0 .

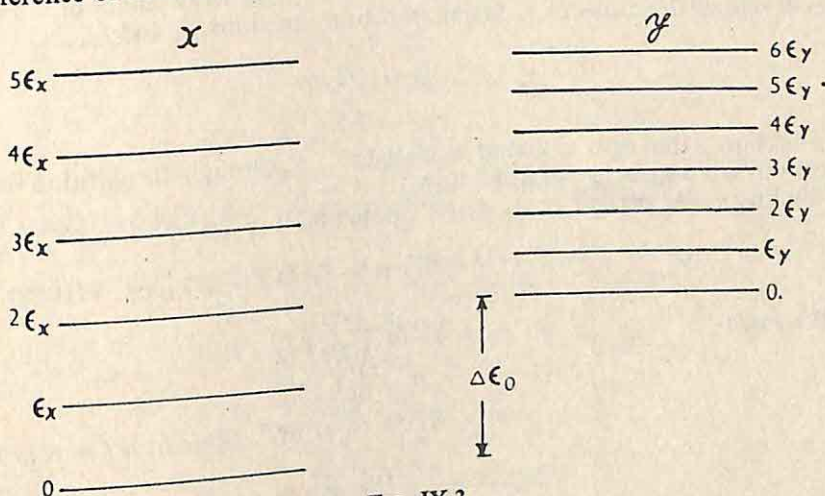


FIG. IX.3

[The multiplicity of the energy-levels has been ignored for the sake of simplicity. It is also necessary to remember that the energy-terms ϵ_x, ϵ_y , etc. include translational, rotational, vibrational and electronic energies and need not be equispaced.]

Let N_x be the total number of molecules of X at eqm. of which N_0^x are present at the ground state. The number of molecules of X in the i th energy level is

$$N_i^x = N_0^x e^{-i\epsilon_x/kT} \quad (\text{Boltzmann})$$

Hence, the total number of molecules of X is given by

$$\begin{aligned} N_x &= N_0^x + N_1^x + N_2^x + N_3^x + N_4^x + \dots \\ &= N_0^x + N_0^x e^{-\epsilon_x/kT} + N_0^x e^{-2\epsilon_x/kT} + N_0^x e^{-3\epsilon_x/kT} + \dots \\ &= N_0^x [1 + e^{-\epsilon_x/kT} + e^{-2\epsilon_x/kT} + e^{-3\epsilon_x/kT} + \dots] \\ &= N_0^x \sum_{i=0}^{\infty} e^{-i\epsilon_x/kT} \end{aligned}$$

Similarly, for the Y -isomeric molecules, we have

$$N_y = N_0^y \sum_{i=0}^{\infty} e^{-i\epsilon_y/kT}$$

At eqm., the population in the ground states of x -levels and of y -levels are also related by the Boltzmann expression, as

$$N_0^y = N_0^x e^{-\Delta\epsilon/kT}$$

Substituting,
$$N_y = N_0^x e^{-\Delta\epsilon_0/kT} \sum_{i=0}^{\infty} e^{-i\epsilon_y/kT}$$

Hence
$$\frac{N_y}{N_x} = e^{-\Delta\epsilon_0/kT} \frac{\sum_{i=0}^{\infty} e^{-i\epsilon_y/kT}}{\sum_{i=0}^{\infty} e^{-i\epsilon_x/kT}}$$

Now, the eqm. constant (K) for the reaction,

$$K = \frac{P_y}{P_x}, \quad \text{where } P_y, P_x \text{ are the partial pressure at eqm.}$$

$$\text{or} \quad K = \frac{P_y}{P_x} = \frac{N_y}{N_x} = e^{-\Delta\epsilon_0/kT} \left[\frac{\sum e^{-\epsilon_y/kT}}{\sum e^{-\epsilon_x/kT}} \right]$$

$$\text{or} \quad K = e^{-\Delta E_0/RT} \left[\frac{\sum e^{-\epsilon_y/kT}}{\sum e^{-\epsilon_x/kT}} \right] \quad \dots (A)$$

It shows that the eqm. constant depends only on the energy values of the different energy-levels of the molecules. Using partition functions, f_y and f_x ,

$$K = e^{-\Delta E_0/RT} \frac{f_y}{f_x}$$

This shows that eqm. constant is related to ΔE_0 through the partition functions. The procedure may be generalised now.

We know, for perfect gases, Gibb's potential is given by

$$G = F + PV = F + RT = -kT \ln Z + RT, \text{ (eqn. VIII.22).}$$

We have

$$\begin{aligned} G &= -kT \ln \left(\frac{f^N}{N!} \right) + kT \\ &= -RT \ln \frac{f^N}{N} + RT \quad [\text{Since } \ln N! = N \ln N - N] \\ &= -RT \ln \left(\frac{f}{N} \right), \quad \dots (a) \end{aligned}$$

The total energy of a molecule,

$$\epsilon = \epsilon_{tr} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{elec} + \epsilon_0$$

where ϵ_0 is the zero-energy, i.e., the energy possessed by the molecule at the ground state at $T = 0^\circ\text{K}$. Usually the zero of energy to which all other energies are referred is the energy of dissociated atoms infinite distance apart, at $T = 0^\circ\text{K}$. The molecule at 0°K would possess some energy, which is the zero-energy, ϵ_0 .

The molecular partition function of a gas is then

$$f^0 = f_{tr}^0 \times f_{rot}^0 \times f_{vib}^0 \times f_{elec}^0 \times e^{-\epsilon_0/kT}$$

$$\text{or} \quad f^0 = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot V \times f_{int}^0 \times \phi_0$$

$$\text{where} \quad \phi_0 = e^{-\epsilon_0/kT} \quad \text{and} \quad f_{int}^0 = f_{rot}^0 \times f_{vib}^0 \times f_{elec}^0$$

$$\text{Putting} \quad \frac{(2\pi mkT)^{3/2}}{h^3} \cdot f_{int}^0 = f', \text{ we may write}$$

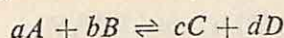
$$f^0 = f' V \cdot \phi_0$$

$$\text{Substituting this in (a) above,} \quad G = -RT \ln \left(\frac{f' V \phi_0}{N} \right)$$

At the standard state, where $P = 1$, we have

$$G^0 = -RT \ln \frac{f' RT}{N} \phi_0 = -RT \ln (f' kT \phi_0) \quad \dots (b)$$

Let us now consider a gaseous reaction,



in which
$$\Delta G^\circ = cG_C^\circ + dG_D^\circ - aG_A^\circ - bG_B^\circ$$

$$\therefore \text{From (b) above, } \Delta G^\circ = -RT \ln \left[\frac{f'_C \times f'_D}{f'_A \times f'_B} \cdot (kT)^{\Delta n} \phi_o^{\Delta n} \right]$$

where
$$\Delta n = (c+d) - (a+b)$$

and
$$\phi_o^{\Delta n} = \frac{\phi_o^c \times \phi_o^d}{\phi_o^a \times \phi_o^b}$$

But,
$$\Delta G^\circ = -RT \ln K_P \quad \dots (IX.13)$$

Hence, the eqm. constant,
$$K_P = \frac{f'_C \times f'_D}{f'_A \times f'_B} \times \phi_o^{\Delta n} \times (kT)^{\Delta n}$$

$$= \frac{f'_C \times f'_D}{f'_A \times f'_B} \times e^{-\Delta \epsilon_o / kT} \times (kT)^{\Delta n}$$

i.e.,
$$K_P = \frac{f'_C \times f'_D}{f'_A \times f'_B} \times e^{-\Delta E / RT} \times (kT)^{\Delta n} \quad \dots (IX.22)$$

And
$$K_C = K_P (RT)^{-\Delta n} = \frac{f'_C \times f'_D}{f'_A \times f'_B} \cdot e^{-\Delta E_o / RT} \cdot \left(\frac{1}{N} \right)^{\Delta n}$$

We may illustrate this with a few simple examples.

(i) Consider the dissociation equilibrium, $I_2 \rightleftharpoons 2I$, in which the eqm. constant can be statistically expressed as

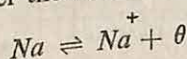
$$K_P = \frac{f'_I}{f'_{I_2}} (kT) e^{-\Delta E_o / RT} = \frac{f'_{I(tr)}}{(f'_{tr} \cdot f'_{vib} \cdot f'_{rot} \cdot f'_{elec})_{I_2}} \times (kT) (e^{-\Delta E_o / RT})$$

$$= \frac{[g_I (2\pi m_I kT)^{3/2} / h^3]^2 [kT] \cdot e^{-\Delta E_o / RT}}{g_{I_2} [(2\pi m_{I_2} kT)^{3/2} / h^3] [8\pi^2 I kT / \sigma h^2] e^{-\frac{1}{2} h\nu / kT} (1 - e^{-h\nu / kT})^{-1}}$$

$$= \frac{g_I^2}{g_{I_2}} \cdot \frac{(\pi m_I kT)^{3/2}}{4\pi^2 I h} (1 - e^{-h\nu / kT}) e^{\frac{1}{2} h\nu / kT} \cdot e^{-\Delta E_o / RT}$$

Where g_I, g_{I_2} are the statistical weight factors, $\sigma = 2$, $m_{I_2} = 2m_I$ and all the entities are supposed to be in their ground states. The magnitudes of I , ν and ΔE_o are all determinable from spectroscopic measurements. The equilibrium constant can thus be obtained in terms of spectroscopic constants only.

(ii) Let us next consider the ionisation of sodium vapour.



From equation (IX.14),
$$K_P = \frac{f_{Na^+} \cdot f_e}{f_{Na}} \cdot kT e^{-\Delta E_o / RT}$$

$$* \phi_o^{\Delta n} = \phi_o^c \times \phi_o^d / \phi_o^a \cdot \phi_o^b = e^{-[c\epsilon_{oC} + d\epsilon_{oD} - a\epsilon_{oA} - b\epsilon_{oB}] / kT}$$

$$= e^{-\Delta \epsilon_o / kT} = e^{-\Delta E_o / RT}$$

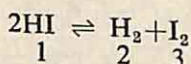
In this case, only the translational motion is concerned, hence

$$K_P = \frac{g_{\text{Na}^+} \cdot g_\theta}{g_{\text{Na}}} \cdot \frac{[(2\pi m_+ kT)^{3/2}/h^3] [(2\pi m_\theta kT)^{3/2}/h^3]}{[(2\pi m_{\text{Na}} kT)^{3/2}/h^3]} \times (kT) e^{-\Delta E_0/RT}$$

$$= \frac{g_{\text{Na}^+} \cdot g_\theta}{g_{\text{Na}}} \cdot \frac{(2\pi m_\theta kT)^{3/2}}{h^3} \cdot (kT) e^{-\Delta E_0/RT}$$

where m_θ = mass of electron, ΔE_0 = the difference of energy of Na-atom and that of Na^+ and electron θ in ground electronic states i.e., $\Delta E_0 = V_i \cdot \epsilon$ where V_i is the ionisation potential and ϵ , electronic charge.

(iii) In the reaction,



let the three entities of substances be symbolised as 1, 2, 3 as above

$$K_P = \frac{f_2 f_3}{f_1^2} e^{-\Delta E_0/RT}$$

Assuming non-degeneracy and also that the entities are in ground electronic state, [See also Sec. VIII.9 and 10],

$$K_P = \frac{(f_{1r_2} \cdot f_{1rot_2} \cdot f_{1vib_2}) (f_{1r_3} \cdot f_{1rot_3} \cdot f_{1vib_3})}{(f_{1r_1} \cdot f_{1vib_1} \cdot f_{1rot_1})^2} e^{-\Delta E_0/RT}$$

$$= \left(\frac{m_2 m_3}{m_1^2} \right)^{3/2} \left(\frac{\sigma_1^2}{\sigma_2 \sigma_3} \right) \left(\frac{I_2 I_3}{I_1^2} \right) \cdot \frac{(1 - e^{-h\nu_1/kT})^2 e^{-\Delta E_0/RT}}{(1 - e^{-h\nu_2/kT}) (1 - e^{-h\nu_3/kT})}$$

The spectroscopic data thus enables one to calculate the eqm. constant.

The entropy of a monatomic gas or vapour, in which the translational partition function need only be considered, is

$$S_T = R \left[\ln \frac{g(2\pi M kT)^{3/2}}{N^{3/2} h^3} \cdot \frac{kT}{P} + 5/2 \right]$$

At standard pressure, $P = 1$, we have,

$$S_T = \frac{5}{2} R + \frac{5}{2} R \ln T + R \ln \frac{g(2\pi M kT)^{3/2} k}{N^{3/2} h^3}$$

But from classical thermodynamics, we know (Sec. IV.48),

$$S_T = \frac{5}{2} R + \frac{5}{2} R \ln T + 2.303 R \times i, \quad (i = \text{vap-pressure constant.})$$

Comparing, $i = \log_{10} \frac{(2\pi M kT)^{3/2} k}{N^{3/2} h^3}$

The values of vapour pressure constant (i) and those of entropy (S) as determined from thermal data and calculated from statistical formulae in a few cases are given below. They exhibit remarkable identity.

TABLE

Substance	i		S	
	Obs.	Calc.	Obs.	Calc.
Zn	1.20	1.18	38.5	38.4
Mg	0.54	0.49	35.3	35.5
Cu	1.40	1.11	37.8	39.7

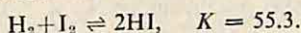
The calculated values of ' i ' may be profitably used in evaluating van't Hoff integration constant ' I ' and this in its turn would enable us to calculate the equilibrium constant of a gaseous reaction [Sec. IX.12, eqn. (XII)].

References for further reading

- (i) *The principles of chemical equilibrium* : DENBIGH
- (ii) *Kinetics of chemical change in gaseous systems* : HINSHELWOOD
- (iii) *Thermodynamics* : LEWIS AND RANDALL
- (iv) *Thermodynamics for chemists* : GLASSTONE
- (v) *Chemical thermodynamics* : ROSSINI

Problems

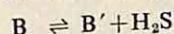
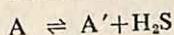
1. At 427°C, for the gaseous reaction



(a) What weight of HI will be formed at eqm. if 1 mole of H_2 and 1 mole of iodine be placed in a 1-litre vessel at 427°C?

(b) Will there be any reaction at 427°C in a mixture consisting of 0.70 atm of HI and 0.02 atm of each of H_2 and I_2 ? If so, will HI be consumed or formed?

2. Two solid compounds A and B dissociate at 20°C into gaseous products, as,



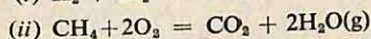
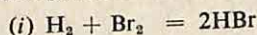
The pressure at 20°C over excess solid A was 50 mm and over excess solid B was 68 mm. Find (i) dissociation constants of A and of B. (ii) the relative number of moles of A' and B' in the vapour over a mixture of the solids. Show that the total pressure of gas over the solid mixture will be 84.4 mm.

3. For the reaction, $\text{F}_2 \rightleftharpoons 2\text{F}$

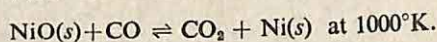
(i) Calculate the degree of dissociation and density of fluorine at 0.4 atm and 1000°K, when $K_P = 1.4 \times 10^{-2}$ atm.

(ii) Calculate also ΔH° for the dissociation of fluorine, if $K_{P_{760}^\circ} = 2 \times 10^{-5}$ atm and $K_{P_{960}^\circ} = 4 \times 10^{-3}$ atm.

4. Calculate the eqm. constants of the following reactions at 25°C using standard heats of formation and third law entropies from tables :

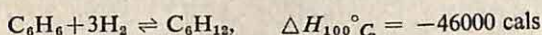


5. Calculate ΔH° , ΔG° , ΔS° for the reaction



Given $K_{P_{950}^\circ} = 4.6 \times 10^3$, $K_{P_{1025}^\circ} = 2.5 \times 10^3$, $K_{P_{1135}^\circ} = 1.6 \times 10^3$

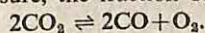
6. In hydrogenation of benzene to cyclohexane



and the partial pressures at eqm. at 100°C and 1 atmosphere are $p_{\text{H}_2} = 1$ mm, $p_{\text{C}_6\text{H}_6} = 69$ mm, $p_{\text{C}_6\text{H}_{12}} = 690$ mm.

Calculate K_P at 100°C and at 90°C. What will be the Gibbs's potential change of the reaction at 100°C?

7. (i) At 1000°C and 1 atm pressure, the fraction of CO_2 dissociated into CO and O_2 is 3×10^{-5} . Calculate K_P for



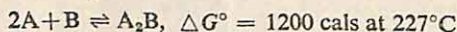
(ii) Oxygen is passed through carbon at 1000°C. At a total pressure of 1 atmosphere, the gaseous mixture is CO = 99.3%, CO_2 = 0.7% by volume, oxygen present is negligible. Determine K_P and the Gibbs's potential change at 1000°C for the reaction, $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$

8. In the gaseous reaction, $\text{S}_2 + 2\text{O}_2 \rightleftharpoons 2\text{SO}_2$, the following are given :

$$\Delta H_{298}^\circ = -173000 \text{ cal}, \quad \Delta S_{298}^\circ = -33.6 \text{ e.u.}, \quad \Delta C_P^\circ = -1.49 + 1.42 \times 10^{-3} T$$

Find the value of K_P at 1000°K.

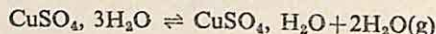
9. In the gaseous reaction,



What total pressure would be necessary to produce 60% conversion of B into A_2B when 2 : 1 mixture is used?

10. In the reaction, $\text{CH}_3\text{COOH} + \text{C}_5\text{H}_{10} \rightleftharpoons \text{CH}_3\text{COOC}_5\text{H}_{11}$, when 3×10^{-4} mole of acid and 4×10^{-4} mole of amylene are mixed in 850 c.c. of an inert solvent, 1.3×10^{-4} mole of ester is formed. How much ester will be formed if 0.004 moles of amylene and 0.002 moles of acid be mixed in a litre?

11. In the reaction,



the dissociation pressure is 7×10^{-3} atm at 25°C and $\Delta H^\circ = 27000$ cal. What will be the dissociation pressure at 127°C ?

12. The following heats of formation (ΔH°) and absolute entropies (S°) are known :

	ΔH° (cals)	S° (eu)
H_2	—	31.2
H_2O	-57800	45.1
CO	-26420	47.3
CO_2	-94040	51.0

Calculate K_P for the reaction, $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ at 500°K assuming ΔH° values being independent of temperature.

13. At 100°C the vapour density of nitrogen tetroxide is 25 at 1 atm. Show that the eqm. constant of the reaction, $K_P = 9.6$.

14. In the isotopic eqm., $\text{HOH} + \text{DOD} \rightleftharpoons 2\text{HOD}$, show that

$$K_P = [m_{\text{HOD}}/(m_{\text{HOH}} \cdot m_{\text{DOD}})] [\sigma_{\text{HOH}} \cdot \sigma_{\text{DOD}}/\sigma_{\text{HOD}}^2] [I_{\text{HOD}}^2/(I_{\text{HOH}} I_{\text{DOD}})] e^{-\Delta E_0/RT}$$

assuming absence of any excitation of vibrational levels.

15. At 2000°K , ΔG for the reaction $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ is given by $\Delta G^\circ = 22000 - 2.5 T$. Estimate K_P at 2000°K .
[Ans. $K_P = 1.4 \times 10^{-2}$].

EQUILIBRIA IN HETEROGENEOUS SYSTEMS : THE PHASE RULE

X.1. The Heterogeneous Systems. When a system consists of parts which have different physical properties (perhaps also different chemical properties) and which are separated by bounding surfaces, the system is said to be a heterogeneous one. When the chemical or physical reactions which occur involve a movement from one state to another state of aggregation, *i.e.*, from one phase to another ; the equilibrium attained is spoken of as heterogeneous. Such equilibria therefore occur in vaporisation, condensation, dissolution, precipitation, transition of one form into another ($S_\alpha \rightarrow S_\beta$), distribution of solids between two immiscible solvents, chemical changes having reactants and resultants in different states of aggregation etc. The study of equilibria in heterogeneous systems is usually made with the help of four general principles all of which are derived from thermodynamics. These principles are (i) the law of mass action (ii) Clapeyron equation (iii) Nernst distribution law and (iv) the Phase Rule. Of these, we are already familiar with the application of the first two.

When information regarding the quantitative relation between reacting species is required, the application of the mass action law is inescapable whether the system is homogeneous or heterogeneous. In Section IX.4 we have seen how the chemical equilibrium in heterogeneous systems is studied with the help of this law.

In a heterogeneous system, the constituents would occur in more than one state or phase, say liquid and vapour. A change in temperature of the system would alter the pressure and the concentrations. A quantitative measure of the alteration in pressure due to variation in temperature for the change of state or transition is given by Clapeyron equation (Sec. IV.45).

$$\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)}$$

or by the Clausius-Clapeyron equation in the integrated form for liquid-vapour equilibrium

$$\ln \frac{P_2}{P_1} = - \frac{L}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

It is easy to see how with these relations, the influence of temperature or pressure on the equilibrium of a heterogeneous system can be studied.

In this chapter, we shall deal with the other two laws—the Distribution Law and the Phase Rule.

THE DISTRIBUTION LAW

X.2. Solubility of a Gas in a Liquid : Henry's Law. The solubility of a gas in a given liquid depends upon the pressure and the temperature. Le Chatelier's principle predicts that with increase of pressure the solubility will increase. Consider a system at equilibrium containing a gas in contact with its solution in a given solvent. If the pressure is increased, the system will tend to reduce the intensity of the stress. The pressure exerted upon the gas will be reduced by any change which reduces the volume. Since the solution of a gas reduces the total volume of the system, it follows that an increased solubility will result from an increase of pressure. It is indeed found to be true.

William Henry, as early as in 1803, made a systematic investigation of the solubility of a gas in a liquid and established that "*the mass of gas (m) dissolved*

by a unit volume of a liquid is proportional to the pressure (p) of the gas, at constant temperature, i.e.,

$$\frac{m}{p} = \text{constant} = K_1 \quad \dots (X.1)$$

This is Henry's Law. It may be stated in another form also. The mass of gas (m) dissolved in unit volume of the solution is really proportional to its concentration (C_2) in solution, whereas the pressure p of the gas is given by $p = C_1 RT$, [C_1 being its concentration in the gas phase]. Hence

$$K_1 = \frac{m}{p} = \frac{k' C_2}{C_1 RT}$$

$$\text{i.e., at const. temperature,} \quad \frac{C_2}{C_1} = K \text{ (constant)} \quad \dots (X.2)$$

In other words, the concentrations in the gas and solution phases bear a constant ratio to one another at a constant temperature.

If instead of mass or concentration we consider the volume of the gas dissolved, we have $m = \frac{M}{RT} pv = k' pv$, where v is the volume of gas dissolved per unit volume of the solution. So,

$$K_1 = \frac{m}{p} = \frac{k' pv}{p}; \quad \text{or} \quad v = \frac{K_1}{k'} = \text{constant} \quad \dots (9.3)$$

i.e., the volume of gas absorbed is independent of pressure.

The solubility of a gas in a liquid is often expressed in terms of absorption coefficient (α) which is defined as the volume of a gas in c.c. (reduced to 0°C) and 760 mm) dissolved in one c.c. of the liquid at the given temperature, when the partial pressure of the gas is 760 mm.

Sometimes the solubility is also given as solubility coefficient (β) which is the volume of gas in c.c. dissolved in 1 c.c. of the liquid the volume being measured at eqm. temperature T and partial pressure P . The absorption coefficients of some gases in water and alcohol are given here.

SOLUBILITY OF GASES

Gases	In water		In ethyl alcohol	
	α_0°	α_{25}°	α_0°	α_{25}°
CO ₂	1.713	0.759	4.44	2.79
N ₂	0.0232	0.0147	—	0.1312
O ₂	0.0489	0.0285	0.2337	0.2171
H ₂	0.0215	0.0178	—	—

Problem : Calculate the volume of nitrogen dissolved per litre of water in eqm. with air at 20°C , the partial pressure being 0.80. Given Henry's law constant $K = P_{N_2}/X_{N_2} = 8 \times 10^4$, where X_{N_2} is expressed in mol-fractions.

$$\text{The mol-fraction} \quad X_{N_2} = \frac{P_{N_2}}{K} = \frac{0.8}{8 \times 10^4} = 1 \times 10^{-5}$$

$$\text{i.e.,} \quad \frac{n_{N_2}}{n_{N_2} + \frac{1000}{18}} = 1 \times 10^{-5}, \text{ when } n_{N_2} = 5.56 \times 10^{-4} \text{ moles}$$

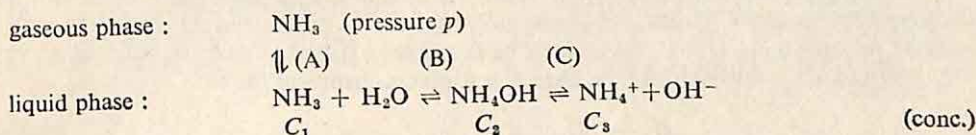
$$\therefore \text{Volume of } N_2 \text{ dissolved per litre} = 5.56 \times 10^{-4} \times 22400 = 12.45 \text{ c.c. at N.T.P.}$$

Henry's law has been found to be satisfactorily obeyed in many cases, especially at low pressures and where the gas and the solution behave ideally.

When several gases from a mixture are simultaneously being dissolved in a solvent, equation (X.1) is valid independently for each gas, p being the partial pressure of the gas considered. The Henry's law constant, K_1 , is different for different gases.

There are however numerous examples known where experimental results diverge widely from the requirements of Henry's law. For the Henry's law to hold good, it is essential that the molecular species in the gas and in the solution phases must be the same. The deviation from Henry's law therefore occurs when the gas molecules in solution undergo association or dissociation. The law also fails when the gases or their solutions behave non-ideally, which is often the case where the solubility is very high. For example, the solubility of HCl gas in water is not governed by Henry's law. HCl gas is highly soluble and the concentrated solution departs considerably from ideal behaviour. Moreover almost the whole of HCl in solution breaks up into H^+ and Cl^- ions.

The dissolution of ammonia gas in water also does not obey Henry's law as given in equations (X.1 and X.2). On dissolving, a major portion of ammonia molecules unite with H_2O to form NH_4OH molecules. A portion of the latter again dissociates into NH_4^+ and OH^- ions. In solution therefore, we have NH_3 molecules, NH_4OH molecules and NH_4^+ ions and the following equilibria exist :



Let p = partial pressure of ammonia,

C = total conc. of ammonia in soln. analytically determined such that

$C = C_1 + C_2 + C_3$, which are conc. of NH_3 , NH_4OH , and NH_4^+ respectively.

$\therefore$ Conc. of undissociated ammonia = $C_1 + C_2 = C - C_3$

and degree of dissociation, $\alpha = \frac{C_3}{C}$, or $C_3 = \alpha C$

In accordance with Henry's law, $\frac{p}{C}$ should be a constant, but this is not experimentally

observed to be so, due to dissociation occurring in solution. Now, in the strict sense $\frac{p}{C_1}$ should

be a constant = K

Again, from eqm. (B), $C_2 = k' C_1$, taking C_{H_2O} as constant.

$\therefore C_1 + C_2 = C_1 + k' C_1 = C_1(1 + k') = k'' C_1$

Hence $\frac{p}{C_1 + C_2} = \frac{p}{k'' C_1} = \frac{K}{k''} = k'''$ should be a constant.

or $k''' = \frac{p}{C_1 + C_2} = \frac{p}{C - C_3} = \frac{p}{C - \alpha C} = \frac{p}{C(1 - \alpha)}$

It is seen that although p/C varies with concentration, $p/C(1 - \alpha)$ should be a constant. This is indeed confirmed from experiments ; α is measured from electrical conductance :

NH_3 in water ($100^\circ C$)		
C	p (mm.)	$P/C(1 - \alpha)$
7.05×10^{-4}	12.9	185
3.53 "	6.4	185
0.214 "	0.367	185
0.107 "	0.178	186

The influence of temperature on solubility may also be easily found out. In general, the solubility of a gas in a liquid decreases with rise in temperature.

It is thus an exothermic process. At a given pressure p , if m_1 and m_2 be the masses of gas dissolved per unit volume of the liquid, at temperatures T_1 and $T_2^\circ\text{K}$, then,

$$m_1/p = K_1 \quad \text{and} \quad m_2/p = K_2$$

$$\therefore \frac{K_1}{K_2} = \frac{m_1}{m_2} = \frac{C_1}{C_2}$$

If ΔH be the heat-change in the process of solution, supposed to be constant, then applying the isochore-relation, we have

$$\ln \frac{K_1}{K_2} = -\frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

This is the quantitative relation between Henry's law constant and temperature.

X.3. The Distribution Law. Henry's law is indeed a particular illustration of a broad general principle called the Distribution Law established theoretically and also experimentally by Nernst.

We have seen in Section IV.57 that if a substance be present in different phases in a system at equilibrium, its chemical potential (*i.e.*, the partial molal thermodynamic potential) in every phase must be the same. If two phases at eqm. in a system be denoted with suffix I and II, then for a given component,

$$\bar{G}_I = \bar{G}_{II}, \quad \text{or} \quad \mu_I = \mu_{II} \quad \dots \text{(IV.108)}$$

Now consider a liquid-liquid system, say water and chloroform, to which some iodine is added. Iodine will dissolve partly in water and partly in chloroform. The two solutions of iodine will separate at eqm. into two layers. The concentrations in the two layers are, of course, different. But the chemical potential of iodine in the two layers is the same. For iodine,

$$\mu_{\text{in water}} = \mu_{\text{in chloroform}}$$

Expressing chemical potential in terms of activities, we have

$$RT \ln a_I + Z_I = RT \ln a_{II} + Z_{II} \quad (\text{Z-terms are constants})$$

$$\text{or at const. temperature,} \quad \frac{a_I}{a_{II}} = K \text{ (constant)} \quad \dots \text{(X.4)}$$

That is, if the activity of a component in one phase is fixed, its activity in another phase at eqm. is also fixed. In dilute solutions or in ideal solutions, the activities may be replaced by concentrations. So that

$$\frac{a_I}{a_{II}} = \frac{C_I}{C_{II}} = K \quad \dots \text{(X.5)}$$

where K is called the *Distribution coefficient* or *Partition coefficient* of the solute between the two solvents at the given temperature.

The concentrations of a solute distributed between two phases at eqm. at a constant temperature bear a fixed ratio. This is Nernst Distribution Law.

It is hardly necessary to mention that it is the ratio of concentration that matters and not the ratio of total amounts of the solute. Of course, the same units of concentration must be used for each solvent.

Henry's law as algebraically represented by eqn. X.2 is the same as eqn. X.5 and so conforms to the Distribution law as applied to the distribution of a component in a gas-liquid system. Or, we may say, the chemical potential in solution and in gas phase being the same,

$$\mu_{\text{gas}} = \mu_{\text{solution}}$$

or

$$RT \ln f + z_g = RT \ln \hat{a} + z_g$$

where f and a are fugacity and activity in the gas and solution phases respectively (eqns. IV.114 and IV.117). Hence, when T is constant,

$$\frac{a}{f} = \text{constant.}$$

In ideal cases, a = concentration (m) ; and f = pressure (p),

i.e., $\frac{m}{p} = \text{constant}$, which is Henry's law.

Nernst also pointed out an important limitation in the distribution law that it is valid only when the molecular species is the same in the two phases. If the solute undergoes dissociation or association in any of the phases, the distribution law as such will not hold good. Thus if a solute remains unaltered in one solvent and undergoes partial dissociation in another, the ratio of total concentrations in the two phases will not be constant, but the ratio of concentrations of undissociated molecules in the two solvents would be fixed. This may be illustrated with some examples.

(a) *Distribution of a solute with same molecular species in two phases.* When iodine is distributed between carbon disulphide and water, or when HgBr_2 is distributed between water and benzene, there is no change in molecular species of the solutes in either solvent, hence

$$K = \frac{C_I}{C_{II}}$$

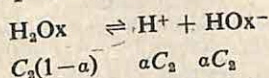
This is confirmed from experimental results.

TABLE

I_2 in CS_2 and H_2O (18°C)			HgBr_2 in water and benzene (20°C)		
I_2 in water gms per c.c., C_2	I_2 in CS_2 gms per c.c., C_1	$K = C_1/C_2$	Conc in water C_1	Conc. in benzene C_2	$K = C_1/C_2$
4.1×10^{-4}	0.174	420	3.2×10^{-3}	3.5×10^{-3}	0.90
3.2×10^{-4}	0.129	400	6.3×10^{-3}	7.15×10^{-3}	0.89
1.6×10^{-4}	0.066	410	11.4×10^{-3}	13.0×10^{-3}	0.88
1.0×10^{-4}	0.041	410	17.0×10^{-3}	19.4×10^{-3}	0.88

Similar cases are found in the distribution of boric acid in water and amyl alcohol, iodine in water and ethyl benzene, phenol in water and amyl alcohol, H_2O_2 in water and ether and so on.

(b) *Distribution of a solute which dissociates in one of the phases.* Such a situation is found in the distribution of oxalic acid between the solvents ether and water. In ether layer the molecules of oxalic acid (H_2Ox) remains unchanged. Suppose its concentration is C_1 . In aqueous layer, oxalic acid suffers dissociation as,



where C_2 is the total concentration of oxalic acid in the aqueous layer and α is the extent of dissociation.

In such a case C_2/C_1 the ratio of total concentrations would not be constant but the ratio of concentrations of undissociated species in the two layers should be constant.

i.e.,
$$\frac{C_2(1-\alpha)}{C_1} = \text{constant.}$$

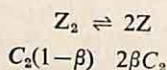
This is confirmed from experimental results given below.

TABLE
DISTRIBUTION OF OXALIC ACID BETWEEN WATER AND ETHER (25°C)*
[$k_a = 5.36 \times 10^{-2}$ ** ; oxalic acid distributed between
50 c.c. water and 200 c.c. ether]

Initial concentration C	Conc. in aq. solution $C_2(1-\alpha)$	$K = \frac{C_2(1-\alpha)}{C_{ether}}$
1.5	0.57	10.49
1.25	0.48	10.54
1.00	0.38	10.49
0.50	0.195	10.50
0.40	0.16	10.54

The degree of dissociation (α) is evaluated from a knowledge of k_a . (eqn. XII.36).

(c) *Distribution of a solute when it associates in one of the phases.* When benzoic acid is added to a mixture of benzene and water, it suffers dimerisation in the benzene layer but in aqueous layer it remains unchanged (very small ionic dissociation being ignored). In the benzene layer, there is an equilibrium between dimers and the monomers, as



If C_2 be the total concentration of the acid in benzene layer and β be the degree to which dimers dissociate into single molecules, then

$$\begin{aligned} \text{conc. of double molecules} &= C_2(1-\beta) \\ \text{and conc. of single molecules} &= 2\beta C_2 \end{aligned}$$

The eqm. constant is

$$K_1 = \frac{4\beta^2 C_2^2}{C_2(1-\beta)} = 4\beta^2 C_2$$

as β is usually very small, i.e.,

$$\beta = \frac{\sqrt{K_1}}{2\sqrt{C_2}}$$

$$\text{The conc. of single molecules in benzene layer} = 2\beta C_2 = \frac{2\sqrt{K_1}C_2}{2\sqrt{C_2}} = k_2\sqrt{C_2}$$

The distribution coefficient will be given by

$$K = \frac{C_{\text{in aqueous layer}}}{C_{\text{in benzene layer}}} \text{ for single molecules}$$

$$\text{or } K = \frac{C_1}{k_2\sqrt{C_2}} \quad \text{or } \frac{C_1^2}{C_2} = \text{constant, when } C_1 = \text{conc. in aqueous layer.}$$

The experimental values are given below for this system.

TABLE : DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BENZENE
 $T = 20^\circ\text{C}$

gms of acid per litre in water	gms of acid per litre in benzene	C_B/C_w	$\frac{C_B}{C_w^2} \times 10^{-3}$
2.89	97.0	33.6	13.9
1.95	41.2	21.6	13.4
0.97	10.5	10.8	13.6
0.79	7.3	9.4	14.0

* J. I. C. S., p. 387, 6, 1955 ; ** Darken, J. Am. C. S., 1941, 63, 1007.

In very dilute solutions, the ionic dissociation α in aqueous layer or the degree of dissociation β of dimers in benzene layer will have appreciable values. In such a condition

$$K = \frac{[C_1(1-\alpha)]^2}{C_2(1-\beta)}$$

In concentrated solutions again, α and β are small but then there would be departures from ideality and hence their activities should be determined. It may be remembered that thermodynamically the ratio of activities need be constant.

Many cases are known where the solute is associated in one solvent and dissociated in another. For example, picric acid is dissociated in water but remains as dimers in the layer of benzene. Lithium chloride distributed between water and amyl alcohol, acetic acid or salicylic acid between water and chloroform etc. are other examples.

X.4. Solvent Extraction. The commonest use of the distribution principle is in the extraction of substances by solvents which is often employed both in laboratory and in large scale manufacture. Organic compounds are generally much more soluble in organic solvents like benzene, chloroform, ether etc. than in water and these solvents are immiscible with water. Organic compounds are then quite easily separated from the mixture with inorganic compounds in aqueous medium by adding benzene, chloroform etc.. On shaking these separate into two layers. Since organic compounds have their distribution ratio largely in favour of benzene phase, more of them would pass into non-aqueous layer. Finally this non-aqueous layer is removed and distilled to obtain the purified compound.

In such solvent extraction it is advantageous to use a given volume of the extracting solvent in small lots in successive stages rather than in one whole at a time. Suppose a solute A is present in 100 c.c. water and that 100 c.c. of ether will be used for its extraction and suppose that the distribution coefficient of A between ether and water is 4,

$$i.e., \quad K = \frac{\text{Conc. of } A \text{ in ether}}{\text{Conc. of } A \text{ in water}} = 4.$$

(i) When the whole of 100 c.c. ether is used at a time for extraction, suppose w_e gram of solute pass into ether layer and w_w gram left in aqueous layer, so that

$$\frac{w_e/100}{w_w/100} = 4, \quad i.e., \frac{w_e}{w_w} = 4 \quad \text{or} \quad \frac{w_e}{w_e + w_w} = \frac{4}{5}$$

This means that 100 c.c. ether has separated $\frac{4}{5}$ th or 80% of the solute originally present.

(ii) Now let us use 100 c.c. of ether in two successive extractions, using 50 c.c. each time. Then in the first stage,

$$\frac{w_e/50}{w_w/100} = 4, \quad \text{or} \quad \frac{w_e}{w_w} = 2, \quad \text{or} \quad \frac{w_e}{w_e + w_w} = \frac{2}{3}$$

That is, in the first extraction $\frac{2}{3}$ rd i.e., 66.7% is extracted. Hence $\frac{1}{3}$ rd of the original amount is still retained in aqueous medium. In the second extraction using again 50 c.c. ether, we shall further extract $\frac{2}{3}$ rd of $\frac{1}{3}$ rd i.e., $\frac{2}{9}$ th of the original amount. In other words, in two extractions using the same 100 c.c. ether, we can separate $(\frac{2}{3} + \frac{2}{9})$ or $\frac{8}{9}$ i.e., 88.9% of the original amount of the compound. Thus a two stage extraction is more efficient. If the same 100 c.c. solvent were used in four or five lots, a still greater proportion could be extracted.

A generalised formula can be easily suggested for the amount remaining unextracted after a given number of operations. Let V c.c. of a solution containing

x_0 gms of substance be extracted with L c.c. of a solvent. Let x_1 gms of substance remain unextracted in water layer. Then

$$\text{conc. of the substance in solvent} = \frac{x_0 - x_1}{L}; \text{ and in water} = \frac{x_1}{V}$$

$$\therefore \text{Distribution coefficient, } K = \frac{\frac{x_1}{V}}{\frac{x_0 - x_1}{L}}$$

$$\text{or } x_1 = \frac{KV(x_0 - x_1)}{L} = x_0 \frac{KV}{KV + L}$$

If second extraction again with L c.c. solvent is made, the quantity unextracted would be

$$x_2 = x_1 \cdot \frac{KV}{KV + L} = x_0 \cdot \frac{KV}{KV + L} \cdot \frac{KV}{KV + L} = x_0 \left(\frac{KV}{KV + L} \right)^2$$

Similarly after n -th extraction, the quantity left behind would be

$$x_n = x_0 \left(\frac{KV}{KV + L} \right)^n \quad \dots (A)$$

If the entire quantity of the extracting solvent be used in one lot, then unextracted,

$$x' = x_0 \left[\frac{KV}{KV + nL} \right] \quad \dots (B)$$

Since the quantity within the parentheses is less than unity, (A) is smaller than (B) and x_n will be smaller the greater the value of n . Hence it is more economical to use the solvent in portions.

Problem : The partition coefficient of an alkaloid between chloroform and water is 20, the alkaloid being more soluble in chloroform. Compare the weights of the alkaloid remaining in aqueous solution after 100 c.c. containing 1 gram has been shaken (a) with 100 c.c. chloroform and (b) with two successive quantities of 50 c.c. chloroform.

$$\text{Distribution coefficient } K = \frac{\text{Conc. in water}}{\text{Conc. in chloroform}} = \frac{1}{20}$$

(a) When 100 c.c. chloroform is used in one lot, the amount unextracted,

$$x_u = 1 \times \left(\frac{KV}{KV + L} \right) = \left(\frac{\frac{1}{20} \times 100}{\frac{1}{20} \times 100 + 100} \right) = \frac{5}{105} = 0.0476 \text{ gms.}$$

(b) When 50 c.c. chloroform is used in each of two stages, the amount unextracted,

$$x_u = 1 \times \left(\frac{KV}{KV + L} \right)^2 = \left(\frac{\frac{1}{20} \cdot 100}{\frac{1}{20} \times 100 + 50} \right)^2 = \left(\frac{5}{55} \right)^2 = 0.0083 \text{ gms.}$$

Problem : An organic compound is extracted from aqueous solution with successive quantities of 25 c.c. chloroform. The original volume of solution is 500 c.c. and the distribution coefficient of the compound is 20 between chloroform/water. Calculate the number of extractions needed for at least 95% recovery of the compound.

$$K = \frac{\text{conc. in water}}{\text{conc. in chloroform}} = \frac{1}{20}$$

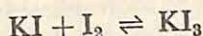
The amount left behind (i.e., 5%) after n -th extraction required for separating the required 95% is given by

$$\frac{5}{100} = \left(\frac{KV}{KV + 25} \right)^n = \left(\frac{\frac{1}{20} \times 500}{\frac{1}{20} \times 500 + 25} \right)^n = \left(\frac{1}{2} \right)^n$$

$$\text{or } n = \frac{\log 5/100}{\log \frac{1}{2}} = 4.3$$

Hence to obtain a minimum of 95% separation we need at least 5 successive extractions.

X.5. Equilibrium Constant from Distribution Coefficient. The knowledge of distribution coefficient is also profitably utilised in the determination of eqm. constant of some reactions when one of the participants is soluble in two immiscible solvents. An apt illustration is the study of equilibrium between iodine and potassium iodide represented as



A solution of KI of known concentration (a) is taken in a stoppered bottle to which some iodine is added, when a portion of the latter combines with iodide to form pot-triiodide. To this is then added some benzene and the mixture is shaken for several hours at constant temperature until equilibrium is reached. On standing the mixture separates into two layers of benzene and water and the concentration of iodine is determined in both the layers by titration against standard thiosulphate. Let

b = conc. of iodine in benzene layer

and c = conc. of iodine in aqueous layer, which really is the sum of concentration of free iodine and KI_3 .

If K be the distribution coefficient of iodine between water and benzene (determined separately), then

$$K = \frac{C_{\text{water}}}{C_{\text{benzene}}} \quad \therefore \text{conc. in water} = K \times \text{conc. in benzene} = K.b$$

Hence the conc. of KI_3 in aqueous layer = $c - Kb$.

$\therefore$ the conc. of KI (free) in aqueous layer = $a - c + Kb$.

We may now say that the equilibrium constant of the reaction,

$$K_{E_q} = \frac{[\text{KI}_3]}{[\text{KI}] [\text{I}_2]} = \frac{c - Kb}{(a - c + Kb)Kb}$$

the square brackets denote the concentrations in water layer.

Since all the quantities on the right-hand side are known, the equilibrium constant is determined.

Other examples of similar application are found in the equilibria :

- | | |
|--|---|
| (a) naphthol + picric acid | $\rightleftharpoons$ naphtholpicrate |
| (b) $\text{CuSO}_4 + 4\text{NH}_3$ | $\rightleftharpoons \text{CuSO}_4 \cdot 4\text{NH}_3$ |
| (c) $\text{Cl}_2 + \text{H}_2\text{O}$ | $\rightleftharpoons \text{HCl} + \text{HClO}$ |
| (d) Aniline + Hydrogen chloride | $\rightleftharpoons$ aniline hydrochloride. (See Sec. XIII.27). |

THE PHASE RULE

X.6. Definitions. The phase rule, put forward by Willard Gibbs (1876) from precise thermodynamical considerations, is the most useful generalisation concerning the equilibria in heterogeneous systems, Gibbs' papers were developed in a mathematical fashion and were published in an obscure journal ; these did not immediately attract notice. It was Roozeboom, Ostwald and van't Hoff who showed the wide possibility of its application and pointed out its unique importance.

The phase rule is a relation between the number of components (C), the number of phases (P) and the variable parameter (F) of a heterogeneous system in equilibrium. It is expressed as

$$F = C - P + 2$$

... (X.6)

It is concerned with effects which changes in pressure, temperature and concentrations will have on the equilibria of heterogeneous systems. The beauty of the Phase Rule lies in its extraordinary simplicity and the capacity of bringing within its ambit most widely divergent and unrelated heterogeneous equilibria.

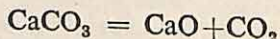
Before we proceed to make an approximate derivation of this principle, it is necessary to define appropriately the terms involved, namely phases, components and degrees of freedom.

Phases : A phase is defined as a physically distinct but homogeneous part of a system separated from other parts by boundary surfaces. A heterogeneous system is therefore composed of two or more phases. Thus a system containing water and its vapour has two phases—the liquid phase and the vapour phase ; each phase is homogeneous and distinct and there is the surface-boundary between the two. A gas mixture is always a single phase. Similarly, all homogeneous solutions are one-phase systems, whatever may be the number of substances present in the same. Every solid, however, constitutes a separate phase. So, when calcium carbonate dissociates into calcium oxide and carbon dioxide, there are two solid phases—viz. calcium carbonate and calcium oxide—and one gas phase of carbon dioxide. That is, it is a three-phase heterogeneous system.

Components : In dealing with the heterogeneous systems, it is necessary to define another term, the components of a system. *The minimum number of independent chemical constituents by which the composition of every phase of the system can be expressed determines the number of components.* It must be clearly understood that the components of a system are not synonymous with the constituents of the system. All the constituents need not be components, but all the components must be included in the constituents.

To illustrate : The system water-water vapour contains only one component. Both the phases may be expressed by one chemical individual namely, H_2O . It is a one-component system. A cane-sugar solution will be a two-component system as there are two independent chemical substances which determine the composition of the solution, namely, H_2O and $C_{12}H_{22}O_{11}$ (cane sugar). Again, ferric chloride and water can give rise to solids like $Fe_2Cl_6 \cdot 12H_2O$, $Fe_2Cl_6 \cdot 7H_2O$, $Fe_2Cl_6 \cdot 5H_2O$, $Fe_2Cl_6 \cdot 4H_2O$ and anhydrous Fe_2Cl_6 , as also the solution, ice and the vapour phase. But to express the composition of any phase, two chemical individuals— H_2O and Fe_2Cl_6 —are only required. It is thus a two-component system.

If a system contains calcium carbonate at a higher temperature, three substances are likely to be present in the system viz, calcium carbonate, calcium oxide and carbon dioxide.



There is however a restriction that the amount of CaO and CO_2 must be equivalent. As such, the composition of any phase can be represented by the concentrations of any two of the three individuals ; say, CaO and CO_2 . The phase calcium carbonate is $lCaO + lCO_2$; the phase calcium oxide is $mCaO + 0CO_2$; and the gas phase carbon dioxide is $mCO_2 + 0CaO$. Hence, although three constituents occur in the system, it is really a two-component system.

As a general rule, the number of components (C) is obtained by subtracting the number of restrictions (q) imposed from the total number of individual constituents (C') present in the system ; i.e., $C = C' - q$. In the case cited above, there are three constituents and one restriction (equivalence of CaO and CO_2), hence the number of components

$$C = 3 - 1 = 2.$$

Likewise in a dilute solution of sugar, there is no restriction and there are two constituents, therefore number of components,

$$C = 2 - 0 = 2.$$

Degrees of Freedom : We shall now consider the general thermodynamic criteria which would govern the equilibria between the different phases of a heterogeneous system. Suppose we are to enquire about the conditions which would keep a liquid in equilibrium with its vapour. It is a well-known observation that if we simply fix the temperature or the pressure, the desired equilibrium will be maintained. This fact may also be thermodynamically arrived at, not only for this system but for any multiphase system which may contain a large number of components. The thermodynamic parameter used to define a heterogeneous system

are the usual pressure, temperature and volume (or concentration) ; other conditions such as gravitational field, magnetic field etc. are not taken into account. In this connection, it would be convenient to introduce a new term, namely the *degrees of freedom*.

If the state of a system cannot be completely defined until at least F data are given, we say that the system has F degrees of freedom. It means that the state of the system depends on F independent variables. *The number of degrees of freedom may then be defined as the number of variables that must be specified in order to define the system completely.* We can also indicate another definition for the number of degrees of freedom. *The number of degrees of freedom of a system is the number of factors (temperature, pressure, concentrations etc.) which can be varied independently without altering the number of phases.* This may be explained with an illustration.

Suppose a gas is enclosed in a cylinder with a movable piston as in Fig. X.1-I. It is a one-phase system. Let the volume of the gas be intentionally kept constant, we can now alter the temperature and pressure without altering the number of phases. Instead, if the temperature be fixed, the other two factors pressure and volume can be varied and therefore the state of the system remains undefined. But if we fix two of the factors—say, temperature and pressure—then the third (volume) is definite. So, by fixing two variable factors, the system is completely defined. Such a system in which two factors can be independently varied without changing the number of phases has two degrees of freedom or it is a bi-variant system.

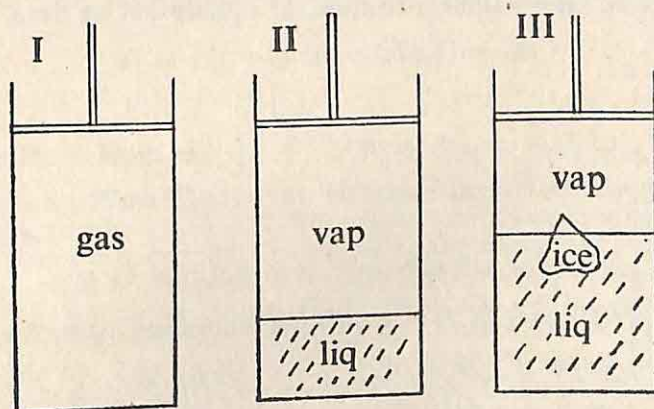


FIG. X.1

Again, suppose a liquid is in contact with its vapour as in Fig. X.1-II. In this case if we fix either the temperature or the pressure, the system is defined completely, subject to the condition of the co-existence of both the phases. For any given temperature, the vapour pressure is immediately fixed. If at a fixed temperature, pressure is altered, one of the phases would disappear. So, this is a system with one independent variable factor or it is a univariant system possessing one degree of freedom.

Further, suppose the system in Fig. X.1-III contains a substance in equilibrium in three phases—say, ice, liquid water and water vapour. This is possible at a particular pressure and temperature. If we vary any one of these factors, either pressure or temperature, one of the phases would disappear. If we lower the temperature, all liquid will solidify and if we raise the temperature the ice will disappear. Hence in this case there is no independent variable or it is a non-variant system, the number of degrees of freedom being zero.

From the thermodynamic standpoint, it would be interesting to find out the independently variable factors or conditions for a number of components existing in equilibrium in different phases. The answer is provided by the Phase Rule.

X.7. The Phase Rule. The phase rule expresses the condition of equilibrium by the relation between the number of the co-existing phases and the components. Consider a heterogeneous system of P number of phases (denoted by superscripts $a, b, \dots p$) containing C number of components (denoted by subscripts 1, 2, 3, $\dots C$) in equilibrium. The concentration of any component in the different phases may be different. The system is a closed one and it is in mechanical and thermal equilibrium, meaning that all the phases are at the same temperature T and under the same pressure P . It may be assumed that there is no chemical reaction between the substances in the system.

The chemical potentials (μ) of the different components in the P -phases are represented as

$$\begin{array}{ll} \mu_1^{(a)}, \mu_2^{(a)}, \dots \mu_C^{(a)}; & \mu_1^{(b)}, \mu_2^{(b)}, \dots \mu_C^{(b)}; \\ \mu_1^{(c)}, \mu_2^{(c)}, \dots \mu_C^{(c)}; \dots & \mu_1^{(p)}, \mu_2^{(p)}, \dots \mu_C^{(p)}. \end{array}$$

Now, imagine small amounts (dn moles) of the components are transferred, under equilibrium conditions, from one phase to another. The following conditions would then hold true.

$$\begin{aligned} dn_1^{(a)} + dn_1^{(b)} + dn_1^{(c)} + \dots dn_1^{(p)} &= 0 \\ dn_2^{(a)} + dn_2^{(b)} + dn_2^{(c)} + \dots dn_2^{(p)} &= 0 \\ \dots &\dots \dots \\ dn_C^{(a)} + dn_C^{(b)} + \dots dn_C^{(p)} &= 0 \end{aligned} \quad \dots (X.7)$$

Further, from Gibbs-Duhem relation, at equilibrium we have,

$$dG = \sum \mu dn = 0.$$

Hence,

$$\begin{aligned} &\mu_1^{(a)} dn_1^{(a)} + \mu_1^{(b)} dn_1^{(b)} + \dots + \mu_1^{(p)} dn_1^{(p)} \\ &+ \mu_2^{(a)} dn_2^{(a)} + \mu_2^{(b)} dn_2^{(b)} + \dots + \mu_2^{(p)} dn_2^{(p)} \\ &+ \dots \dots \dots \\ &+ \mu_C^{(a)} dn_C^{(a)} + \mu_C^{(b)} dn_C^{(b)} + \dots + \mu_C^{(p)} dn_C^{(p)} = 0 \end{aligned} \quad \dots (X.8)$$

Multiplying equations (X.7) by c -different multipliers (λ) we find,

$$\begin{aligned} \lambda_1 dn_1^{(a)} + \lambda_2 dn_2^{(b)} + \dots + \lambda_2 dn_1^{(p)} &= 0 \\ \lambda_2 dn_2^{(a)} + \lambda_2 dn_2^{(b)} + \dots + \lambda_2 dn_2^{(p)} &= 0 \\ \dots &\dots \dots \\ \lambda_C dn_C^{(a)} + \lambda_C dn_C^{(b)} + \dots + \lambda_C dn_C^{(p)} &= 0 \end{aligned} \quad \dots (X.9)$$

Adding the equations (X.8) and (X.9) we can pick up and equate the coefficients of each of the dn -terms to zero. The results would be,

$$\begin{aligned} -\lambda_1 &= \mu_1^{(a)}, & -\lambda_1 &= \mu_1^{(b)}, & \dots & -\lambda_1 &= \mu_1^{(p)} \\ -\lambda_2 &= \mu_2^{(a)}, & -\lambda_2 &= \mu_2^{(b)}, & \dots & -\lambda_2 &= \mu_2^{(p)} \\ &\dots & &\dots & & \dots & \\ -\lambda_C &= \mu_C^{(a)}, & -\lambda_C &= \mu_C^{(b)}, & \dots & -\lambda_C &= \mu_C^{(p)} \end{aligned}$$

$$\begin{aligned} \text{That is, } \mu_1^{(a)} &= \mu_1^{(b)} = \dots = \mu_1^{(p)} \\ \mu_2^{(a)} &= \mu_2^{(b)} = \dots = \mu_2^{(p)} \\ &\dots \dots \dots \\ \mu_C^{(a)} &= \mu_C^{(b)} = \dots = \mu_C^{(p)} \end{aligned} \quad \dots (X.10)$$

These are the equations of the phase equilibrium. Thus, we know from the thermodynamic considerations that at equilibrium the chemical potentials of a

constituent in all the phases of the system must be the same. Different constituents, of course, have different chemical potentials.

Now, let us first determine the total number of variable factors in the given system. So far as the composition variables are concerned, in every phase we may have C -components having C different concentrations. But in a closed system, if we arbitrarily choose concentrations of $(C-1)$ components, the last one is fixed by the remainder. So, there are really $(C-1)$ composition variables in each phase. For all the P -phases, the number of composition variables would be $P(C-1)$. In addition, there are two other variables, namely, temperature and pressure. Hence,

$$\text{the total number of variables} = P(C-1)+2 \quad \dots (X.11)$$

Next let us see how many of these variables are already fixed and cannot be altered. From equations (X.10) it is known that if the chemical potential of a component in any of the P -phases be defined, its chemical potentials in the other $(P-1)$ phases cannot be varied. The chemical potential is related to the concentrations. As such if the concentration of a component in any one phase be arbitrarily fixed, then the concentrations of the same component in the other $(P-1)$ phases would be fixed, i.e., non-variant. For this particular component, $(P-1)$ composition variables are fixed. For all the C -components, the number of composition variables thus immobilised would be $C(P-1)$. If we subtract this number from the total number of possible variables of the system (eqn. X.11), we shall get the number of variables of the system, which can be arbitrarily chosen. This would represent the number of the degrees of freedom (F) of the system.

$$F = P(C-1)+2-C(P-1)$$

or

$$F = C-P+2 \quad \dots (X.12)$$

This is the Phase Rule.

The systems are named univariant, bivariant, trivariant, etc. according as the degrees of freedom are 1, 2, 3, etc. The phase rule takes into account only the variables of temperature, pressure and the composition and the influence of other factors such as electric, magnetic, gravitational, surface forces etc. is ignored. The equation does not depend upon the nature or the amount of the substances. It also does not assume anything regarding the constitution of the matter or the molecular complexity. The Phase Rule tells us that the systems having the same degrees of freedom shall behave in a similar fashion. It thus enables us to classify the states of equilibrium. It is immaterial whether the phase-changes in systems are chemical or physical, if the number of degrees of freedom be the same, the systems shall behave similarly when temperature, pressure and composition (concentrations) are varied.

To illustrate : We may take the following three different systems, namely, (i) Water and its vapour (ii) Solid β -tin and its vapour and (iii) Solid calcium carbonate in contact with its dissociated products calcium oxide and carbon dioxide. The last system involves a chemical reaction while the other two are physical changes. The details of the systems are :

System	Co-existing phases	Number of phases and components	degrees of freedom
Water and vapour	liquid-gas	$P = 2, C = 1$	$F = 1-2+2 = 1$
Tin and its vapour	solid-gas	$P = 2, C = 1$	$F = 1-2+2 = 1$
Calcium carbonate	solids-gas	$P = 3, C = 2$	$F = 2-3+2 = 1$

We have already seen previously that the number of components in the system in which calcium carbonate is dissociated is two.

Now all the systems, in accordance with the phase rule, are univariant and hence all of them are expected to behave similarly. The experimentally observed

variation of vapour pressures with temperatures for the three systems are given in Figs. X.2 (a, b, c).

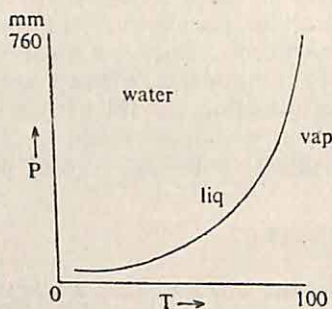
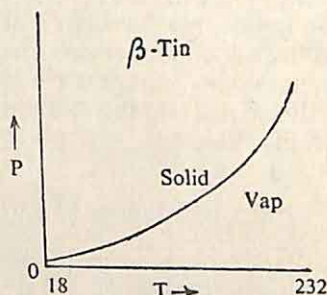
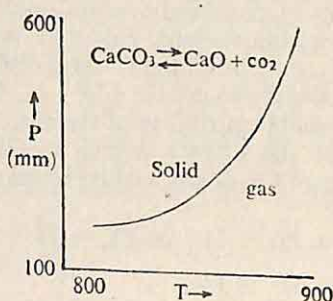


FIG. X.2(a) Water and its vapour



(b) Tin and vapour



(c) Dissociation of CaCO_3

The similarity of the curves indicates that although the systems are widely different yet they behave in like manner. Alternatively, from a knowledge of the degrees of freedom and the number of components present it is possible to predict the number of phases co-existing in the system under equilibrium. Such a study would therefore enable us to state whether a given system is homogeneous or a heterogeneous mixture. With the help of the phase rule we have grouped together widely different phenomena and it guides us to ascertain the existence of a new phase. The law of mass action cannot provide us with such information. When A and B react, the law of mass action would give quantitative relations of the equilibrium concentrations but the law cannot predict if any compound A_xB_y has been formed as a new phase or not. The Phase Rule has been of great value in the practical field such as in the isolation of salts from mixtures, preparation of alloys, etc. It helps in the adjustment of temperature, composition, etc. to obtain a desired product. The preparation of potassium chloride from Stassfurt deposits is an outstanding example.

X.8. The Phase Rule for Systems with Reactive Components. In deducing the equation of the phase rule (eqn. X.12), it was tacitly supposed that the components do not undergo any chemical reaction between them. But in the event of the components (or some of them) undergoing chemical changes between one another, the equation has to be modified. It was seen that at equilibrium, the composition variables were governed by the equality of the chemical potentials of a component existing in different phases (eqn. X.10). Now, if there is a reaction between the components, then apart from the fixed composition variables indicated above, other conditions are also superimposed. For a given concentration of a component involved in a chemical reaction, the concentrations of the other components participating in the same will become fixed or invariant. That amounts to the imposition of some additional restrictions on the composition variables. The number of such restriction depends on the number of reactants and resultants.

If Q denotes such restrictions, the number of degrees of freedom will be diminished by the number Q . Therefore, in such a case, the degrees of freedom will be given by

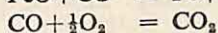
$$F = [C' - P + 2] - Q \quad \dots (X.13)$$

where C' is the total number of constituents in the system.

It means that the general phase-rule equation may be used if we assume in such reactive systems the number of components reduced by the number of restrictions.

That is,
$$F = C - P + 2, \text{ where } C = C' - Q.$$

As an example let us consider a system in which the phase changes are the same as occurring in the upper part of the blast furnace of iron. The iron oxide (Fe_2O_3) is reduced by carbon monoxide. There is no liquid phase. We may consider this as a system containing Fe, FeO, Fe_2O_3 , and CO, CO_2 and air ($\text{O}_2 + \text{N}_2$). The total number of phases in the system is four—one gas phase and three distinct solid phases. There are, however, the following reactions.



There are as many as seven constituents but the number of components, in accordance with the phase rule, will be restricted by three chemical equations. So

$$\text{the number of components} = 7 - 3 = 4$$

The degrees of freedom will be

$$F = C - P + 2 = 4 - 4 + 2 = 2$$

Hence, the system would be bivariant. But if air were absent or only pure oxygen were present (assuming the closed system in eqm.), the system would be univariant.

$$F = 3 - 4 + 2 = 1$$

Besides the chemical reactions, there may arise other conditions which would restrict the number of free variables. For example, if a system be at the critical point, the liquid and vapour phases are identical. In this case, the number of degrees of freedom would be

$$\begin{aligned} F &= C - P + 2 - Q \\ &= 1 - 2 + 2 - 1 = 0 \end{aligned}$$

i.e., the critical state would be an invariant point.

Similarly, in a binary azeotropic liquid mixture, it is found that the compositions of the vapour phase and the liquid phase are the same. Hence there is an identity and so restriction, $Q = 1$. The number of degrees of freedom would be,

$$F = C - P + 2 - Q = 2 - 2 + 2 - 1 = 1$$

The system would be a univariant one. The azeotropic mixture would distil at a fixed temperature when the pressure is maintained constant. (Sec X.19).

X.9. Phase Diagrams. The effect of changes in temperature, or in pressure or composition on the changes of phase in a system can be easily understood only when these are graphically represented. The conditions under which the different phases can co-exist are conveniently described by graphs called phase diagrams. That is why phase diagrams are universally employed in the application of phase rule to heterogeneous systems. When there are only two variables, such as pressure and temperature, or temperature and concentration, rectangular coordinates are used. But when three variables are concerned, solid diagrams are needed. Time is not a variable since phase diagrams are concerned with systems in equilibria. The total quantities of the components are also not of any importance but their concentrations are. A number of phase diagrams of different types will be illustrated in the pages following. But a few elementary facts may be mentioned here.

The effect of pressure on the temperature of transition from one phase to another of a substance is governed by Clapeyron equation.

$$\frac{dP}{dT} = \frac{\Delta H}{T \cdot \Delta V} = \frac{\Delta S}{\Delta V} \quad \dots (X.14)$$

In other words, a plot of P vs T would give the conditions of equilibrium between two phases, say, between gas-liquid, or liquid-vapour, etc. Let us consider the common changes of state :

(a) *Liquid-vapour equilibrium.* In the change of a liquid into vapour, ΔS is positive. Further $V_{\text{vap}} \gg V_{\text{liquid}}$, i.e., ΔV is positive. Hence $\frac{dP}{dT}$ will be a positive quantity i.e., $\frac{\partial P}{\partial T}$ will have a positive slope, as shown in (I) of Fig. X.2d.

The molar entropy change ΔS in vaporisation of a liquid is of the order of 10 e.u. and the volume change 1×10^4 c.c./mole. Hence

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{10}{1 \times 10^4} = 10^{-3} \text{ cal. deg}^{-1} \text{ c.c.}^{-1} \approx 0.04 \text{ atm/deg.}$$

(b) *Solid-vapour equilibrium.* In the sublimation of a solid into vapour, similar conditions prevail. Both ΔS and ΔV are positive, ΔV is practically the same as in case (a), but ΔS would be larger. Hence $\frac{\partial P}{\partial T}$ will be positive and will have a steeper slope compared to that of liquid-vapour equilibrium.

(c) *Solid-liquid equilibrium.* In the fusion of a solid, ΔS is positive. ΔV is also positive in most cases but may also be negative in some cases as in ice-water system. Hence $\frac{dP}{dT}$ may have a positive slope or may have a negative slope.

The value of ΔS in fusion is of the order of 5 e.u. per mole and ΔV is usually of the order of ± 5 c.c. Therefore,

$$\frac{dP}{dT} = \pm \frac{\Delta S}{\Delta V} = \pm 1 \text{ cal c.c.}^{-1} \text{ degree}^{-1} = \pm 40 \text{ atm/degree.}$$

or
$$\frac{\partial T}{\partial P} = \pm 0.02 \text{ degree/atmosphere.}$$

This means that change of 1 atmosphere pressure will cause a change in fusion temperature by only about 0.02 degree. That is the slope of the P - T curve for fusion is very large, almost vertical, as shown in (III) of Fig. X.2d.

This line (III) in the figure is the locus of points (P , T) at which the solid and liquid (s/l) can co-exist. Similarly the other curves I and II indicate the locus of points for co-existence of other phases, l/g and s/g. Points on the right of a line indicates one phase and points on the left another phase.

The point of intersection of any two curves will indicate co-existence of all the three phases solid-liquid-vapour in eqm. The point is called a triple point. We can now consider some simple systems. Phase diagrams are classified on the basis of number of components such as one component system, two component system, etc.

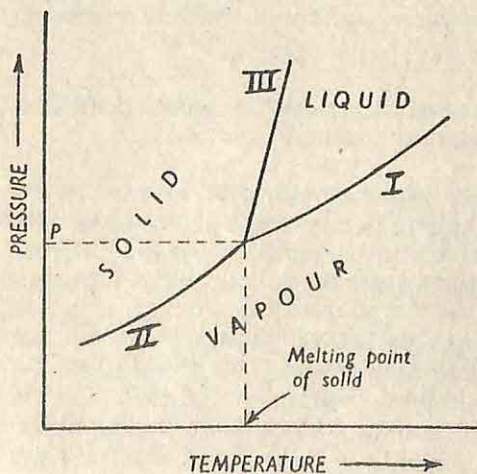


Fig. X.2(d)

ONE COMPONENT SYSTEMS

X.10. The System, H_2O . One component systems shall comprise of a pure substance only. The simplest and a typical example will be that of a system containing water. Under ordinary circumstances there are three possible phases, ice, water and water vapour.

(a) If the system consists of only one phase, say vapour, then

$$F = C - P + 2 = 1 - 1 + 2 = 2 ;$$

the system would be bivariant according to the Phase Rule. That is, both pressure and temperature can be varied simultaneously without any change in its phase or both the pressure and temperature variables must be determined to define the state of the system.

(b) If the system contains two phases in equilibrium, say, water and its vapour, or say ice and water, or ice and vapour, the system would be a univariant one. For

$$F = C - P + 2 = 1 - 2 + 2 = 1,$$

i.e., the equilibrium between the two phases would be known if only the temperature or the pressure be fixed.

The truth of the above predictions of the Phase Rule is borne out by the phase-diagram of water as given in Fig. X.3. The line OA is the vapour-pressure curve for water, the vapour pressure increasing with rise in temperature. The points on this line show the pressure of water vapour under which water and its vapour can exist in equilibrium at different temperatures. This curve OA then represents the univariant states of the system water/vapour. For any given temperature, equilibrium vapour pressure is fixed, *i.e.*, there is one variable only. For any point x above OA , the system would be liquid water. If the pressure is lowered at constant temperature, the vapour phase would appear at the point y . On further lowering of pressure, to z , the system would be completely vapour (temp. remaining constant). Hence OA in the phase diagram is the demarcation or boundary line between two phases, water and its vapour.

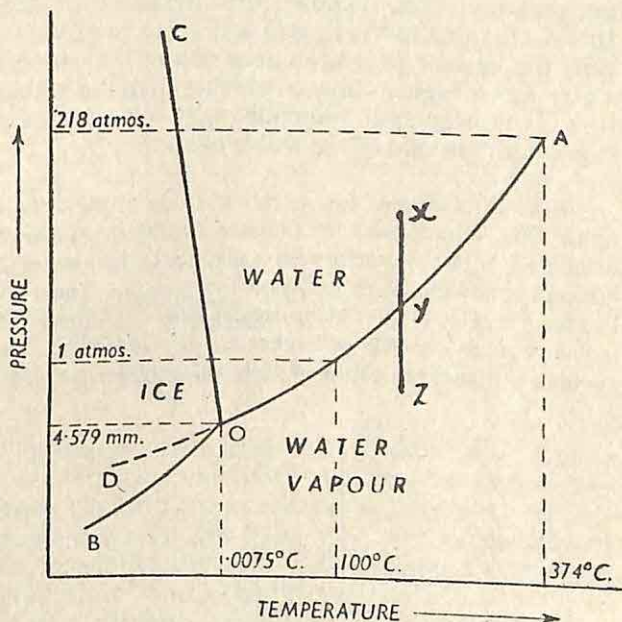


FIG. X.3 The phase-diagram for water (not to scale)

There is however an upper limit for OA terminating at A , its critical state, when the liquid phase is no longer distinguishable from vapour phase. The co-ordinates of A are $p = 218\text{ atm}$ and $t = 374^{\circ}C$.

Similarly the curve OB denotes the vapour-pressure curve of ice or more appropriately the sublimation pressure-temp. curve for ice. It registers the vapour-pressures under which ice is in equilibrium with its vapour at different temperatures. This curve is also the line of demarcation between ice and vapour. The slope of OB is however steeper than that of OA , as has been pointed out in the previous section.

On the other hand, OC is the freezing point curve indicating the equilibria at different temperatures between ice and water. The line has a negative slope, *i.e.*, melting point is lowered with increase in pressure, the density of solid ice being less than that of water.

Each of the three lines OA , OB and OC indicates the two-phase equilibria and represents univariant states. The areas enclosed between these lines represent regions of a single phase *i.e.*, bivariant states of the system. Thus the region AOB is vapour, BOC ice and COA water.

The point O , where the three lines meet, all the three phases, ice, water and vapour should co-exist. This is called a *triple point*. The pressure at this point has been found to be 4.58 mm. The freezing point of water is 0°C under 760 mm pressure, and from Clapeyron equation, the freezing point changes by 1° when pressure is changed by about 140 atmospheres. Hence at 4.58 mm the freezing point will be raised to $+0.0075^{\circ}$. That is, the triple point has $p = 4.58$ mm, $t = 0.0075^{\circ}\text{C}$.*

Since there are three phases, we have

$$F = 1 - 3 + 2 = 0$$

i.e., the system is non-variant at the triple point. If either the temperature or the pressure is changed, the three phases would not co-exist, one of the phases would disappear.

It is however possible to cool water below its freezing point without solidification. The liquid below its freezing point is said to remain in *supercooled state*. This supercooled state is not quite stable and it is usually described as a *metastable state*. The supercooled water has also its vapour pressure which changes with temperature. The vapour pressure curve of supercooled water is given by OD (the dotted line in the figure) which is a continuation of AO . The line OD is above OB , the vapour pressure curve of ice, indicating that the metastable supercooled water has a higher vapour pressure than the stable solid state at a given temperature. It is a general principle, that "*the vapour pressure of the metastable phase is greater than that of the stable phase*".

Different Forms of Ice. A careful study of the freezing of water under very high pressures up to 50000 atmospheres by Tamman and by Bridgman revealed the existence of several forms of ice other than the ordinary ice (called Ice I) there are at least six other forms of ice stable under different conditions of temperature and pressure. These polymorphic forms of ice are called Ice I to Ice VII. (Ice IV, not being satisfactorily confirmed). The different forms of ice differ in crystalline structure, density and other physical properties. The pressures and temperatures governing their existence are indicated in the phase diagram Fig. X.4. These curves reveal that at certain

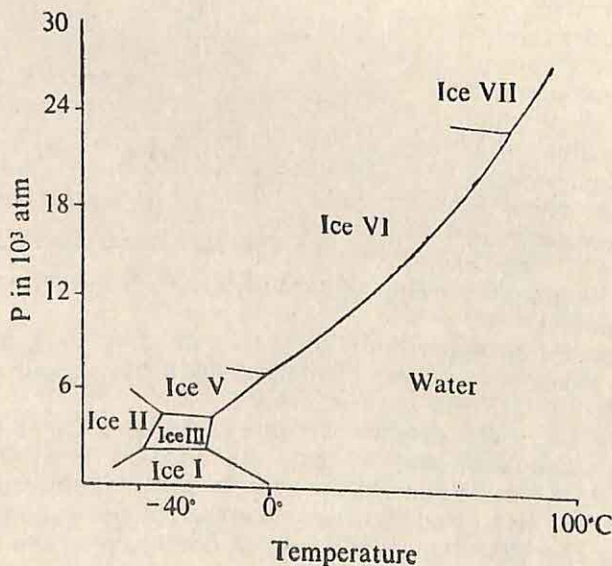


FIG. X.4 The polymorphic forms of Ice (not to scale)

*Pure water actually freezes at 0.0024°C under 1 atmosphere, hence the experimental value of triple point is $0.0075 + 0.0024 = 0.0099^{\circ}\text{C}$.

With these four phases of sulphur, the Phase rule would lead to the following predictions as to the possible systems that would be in equilibrium.

(a) A system with all the four phases cannot exist. For in that case,

$$F = C - P + 2 = 1 - 4 + 2 = -1,$$

the degree of freedom becomes negative, which has no meaning.

(b) There are four possibilities of three phases out of four co-existing at eqm., which are

(i) S_α — S_β —liq (ii) S_α — S_β —vapour (iii) S_α —liq—vapour (iv) S_β —liq—vapour

For each of these systems, $F = C - P + 2 = 1 - 3 + 2 = 0$

i.e., non-variant, in which all parameters are fixed. Hence such systems are represented by points. Four such triple points are thus expected.

(c) Six possible systems of two-phases are realisable, namely

(i) S_α — S_β (ii) S_α —liq. (iii) S_α —vapour

(iv) S_β —liq. (v) S_β —vap. (vi) liquid—vapour.

In each case, $F = C - P + 2 = 1 - 2 + 2 = 1$, the system would be univariant, diagrammatically expressed by six lines.

(d) When only one phase occurs, the system would be bivariant, $F = 2$, and there shall be four areas in the phase diagram to represent the four phases.

All the expectations have been experimentally realised and are shown in the phase-diagram, Fig. X.6.

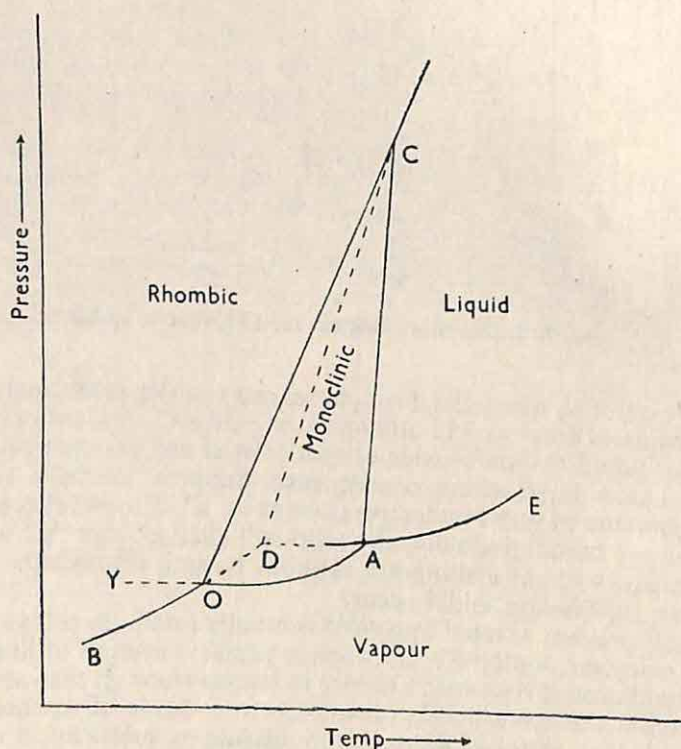


FIG. X.6 Phase diagram of sulphur (not to scale)

Co-ordinates :	Pr.	A	O	C	D
	$t(^{\circ}\text{C})$	0.025 mm 120°	0.01 mm 95.5°	1290 atm 151°	0.03 mm 114°

The curve BO shows the change of vapour-pressure of rhombic sulphur with change in temperature. The curve OA shows the vapour-pressure of monoclinic sulphur at different temperatures. These two curves intersect at O where $t = 95.5^{\circ}\text{C}$. At O , the three phases rhombic, monoclinic solids and the vapour can exist in

equilibrium with one another and this is a triple point for these three phases. This point is also known as the *transition temperature* for the two solid phases $S_a \rightleftharpoons S_\beta$. If S_a be rapidly heated beyond 95.5°C without permitting sufficient time for transformation into S_β , the rhombic sulphur will remain in metastable state and the vapour pressure will change along QD , which is above the curve for stable state OA . With time S_a will change into S_β . Similarly if S_β is cooled below 95.5°C , its vapour pressure will change along OY . S_β is metastable below 95.5°C and will slowly change into S_a . Above the transition temperature one form is stable and below the transition temperature the other form.

The upper limit of the vapour pressure curve of monoclinic sulphur is A , where it melts into liquid sulphur ($p = 0.025$ mm) at 120°C and AE is the vapour pressure curve of liquid sulphur. Since OA and AE intersect at A , the three phases S_β , liquid and vapour can exist in equilibrium at this point. That is, A is a triple point for S_β -liq-vapour.

Again, the change in melting point of monoclinic sulphur into liquid with increase in pressure, governed by Clapeyron relation, is represented by AC . At any point on this line AC , monoclinic and liquid sulphur are in equilibrium forming univariant systems. This is identical to ice-water equilibrium.

Similarly the curve OC indicates the changes in transition temperature of $S_a \rightleftharpoons S_\beta$ with increase in pressure. Every point on this line indicates a univariant system of two solid phases S_a and S_β . The transition of rhombic to monoclinic sulphur is accompanied by an increase in volume, $\Delta v = 0.01395$ c.c./gm. Hence, from Clapeyron equation, transition point is increased by increase of pressure, $\Delta T = 0.04^\circ/\text{atmosphere}$.

At C , where AC and OC intersect, we have a third triple point. At this point S_a , S_β and liquid sulphur can remain in equilibrium with one another, ($p = 1290$ atm., $t = 151^\circ\text{C}$). Beyond this point, the monoclinic sulphur cannot exist. The occurrence of monoclinic sulphur is thus restricted within the region AOC .

Liquid sulphur when supercooled has a vapour pressure curve (for such metastable condition) along AD , a continuation of EA . The vapour-pressure curve of metastable S_a is OD . These two intersect at D , ($t = 114^\circ\text{C}$) where sulphur vapour, liquid sulphur and rhombic sulphur would co-exist. This is the fourth triple point, S_a -liq-vapour. The line DC represents the change of freezing temperature of liquid to rhombic sulphur with increase in pressure. The point D is indeed a metastable triple-point and can be experimentally realised only under carefully manipulated conditions.

There are thus four triple points at O , A , C and at D . The lines representing univariant two-phase systems are BO (S_a/vap), OA (S_β/vap), AE (liq/vap), AC (S_β/liq), OC (S_a/S_β), DC (S_a/liq).

These six lines have divided the whole diagram into four regions of bivariant systems containing a single phase : areas $BOAE$ (vapour), CAE (liquid), COA (S_β), BOC (S_a).

Enantiotropy and Monotropy. Lavoisier recognised that diamond was a form of carbon. The plague of tin was known from very early times. In the last century Mitscherlich prepared sulphur in two distinct forms—rhombic and monoclinic. It was Berzelius who first used the term '*allotropy*' when an element was found to exist in two or more forms possessing different properties. Later Ostwald included compounds also and defined *allotropism* as the phenomenon in which a substance, element or compound, could exist in two or more forms exhibiting different properties, physical or chemical.

In the case of solid allotropes, the term *polymorphism* is more commonly used. A solid which occurs in two forms is said to be *dimorphous*, in three *trimorphous*, etc. Broadly, three types of allotropism are recognised :

(i) Enantiotropy (ii) Monotropy and (iii) Dynamic allotropy.

(i) *Enantiotropy*. When the two forms are stable at different ranges of temperature, it is said to be enantiotropic. Each form is stable in a given temperature range. One form is stable below and the other form above the transition temperature and the transformation from one to the other is reversible. In enantio-

tropic substance the transition point is below the melting point of the substance, and the transition point can be realised under atmospheric pressure. Such cases of enantiotropy are found in S_α and S_β , grey and white tin, ammon. chloride, red and yellow mercuric iodide, etc. The typical vapour pressure curves of the two solid forms and the liquid of an enantiotrope would be of the nature as given in Fig. X.7, in which the data for sulphur have been used.

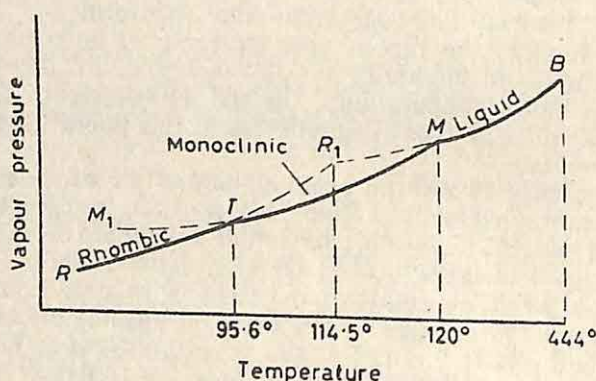


FIG. X.7 Enantiotropy : S_α and S_β (not to scale)

(ii) *Monotropy*. In monotropic substances, one form is metastable and has a tendency to pass into the stable form under all circumstances. The change takes place in one direction and is irreversible. The vapour pressure of the metastable form is higher than that of the stable form (Fig. X.8). The transition temperature T is above the melting point (M_1) of the substance and as such it cannot be experimentally realised under atmospheric pressure. Instances of monotropy are provided by white and red phosphorus, α - and β -benzophenone, aragonite calcite (CaCO_3), etc.

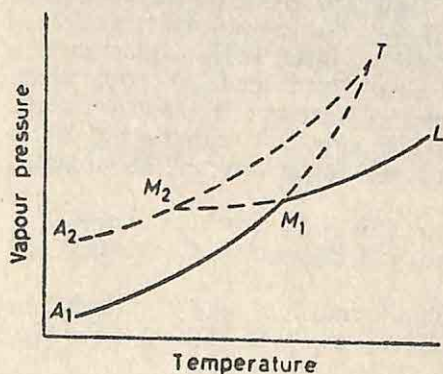


FIG. X.8 Monotropy

M_1L is the vap-pressure curve of liquid. A_2M_2 is the vap-pressure curve of the metastable form melting at M_2 . The point of intersection of A_1M_1 and A_2M_2 (extrapolated) would have been the transition point T but it is higher than m.pt of stable variety and cannot be experimentally determined.

(iii) *Dynamic allotropy*. In dynamic allotropism, two forms remain in the same phase, i.e., the system would be homogeneous either liquid or gaseous. One form changes into the other at exactly the same rate as the reverse process. Both the forms are stable over a considerable range of temperature. There is no transition point, the composition varies with temperature. Such dynamic allotropy is observed with liquid sulphur. On melting, sulphur is present as S_λ . With rise in temperature proportion of the other form S_μ begins to increase. There is an equilibrium, $S_\lambda \rightleftharpoons S_\mu$. In sulphur the dynamic allotropy is supposed to be due to different lattice arrangement. Dynamic allotropism may also arise through polymerism as in oxygen/ozone, or for other reasons, as in ortho/para hydrogen where it is due to opposite spinning of the nuclei.

TWO COMPONENT SYSTEMS

The two component systems may occur in such a large number of types that even a proper and satisfactory classification of these systems seems difficult. We shall consider here some typical and common systems occurring in

- (a) liquid-liquid phases
- (b) liquid-vapour phases
- (c) liquid-solid phases
- and (d) gas-solid phases.

SYSTEMS WITH LIQUID-LIQUID PHASES

When water is added to alcohol, the two liquids are completely miscible in all proportion and form a homogeneous solution. When water is added to, say, nitrobenzene scarcely any nitrobenzene will dissolve in water or any water in nitrobenzene. The two liquids will exist in separate layers; the liquid pair is immiscible. But if we add some phenol to water, first phenol will be dissolved in water but as the amount of added phenol increases, phenol will form a separate layer. In fact the water layer will contain dissolved phenol and the phenol layer will also have appreciable amount of dissolved water. Such liquids are *partially miscible*. When two such partially miscible liquids (*A* & *B*) are brought together in appreciable amounts we have two saturated solutions in two layers—one of *A* in *B* and another of *B* in *A*—at equilibrium. These two solutions are described as *conjugate solutions*.

The study of miscibility of partially miscible liquid pairs are quite interesting. It is usually convenient to study such miscibilities under the external atmospheric pressure which is taken as constant and much higher than the vapour pressure of the components. As such in such studies of miscibility under constant pressure, the vapour phase is ignored. The mutual solubilities of liquids are represented graphically in a temperature-composition diagram.

X.13. System : Phenol and Water. In Fig. X.9, *AB* is the solubility curve of phenol in water. It gives the percentage of phenol dissolved in water at different temperatures, the solubility rising with temperature. On the other hand when water is added to phenol slowly, small amounts of water are immediately dissolved but when the amount of added water is increased, the limit of saturation is reached and water forms a separate layer. The solubility curve of water in phenol is given by *CB*, the solubility again increasing with temperature. The two solubility curves meet at *B* (temp. 66°C, 33% phenol).

At a given temperature (say 40°), if we have *x* percent phenol in water, it will be completely miscible and a homogeneous solution will result. Keeping the temperature constant, if we go on increasing the amount of phenol, the solubility limit *l*₁ will be reached. Any further addition of phenol will give rise to two separate layers; (a) water in phenol layer and (b) phenol in water layer. That is, on the left of *l*₁ a point will correspond to homogeneous solution and on the right a point would indicate existence of heterogeneous system of two layers or phases. This is true for other

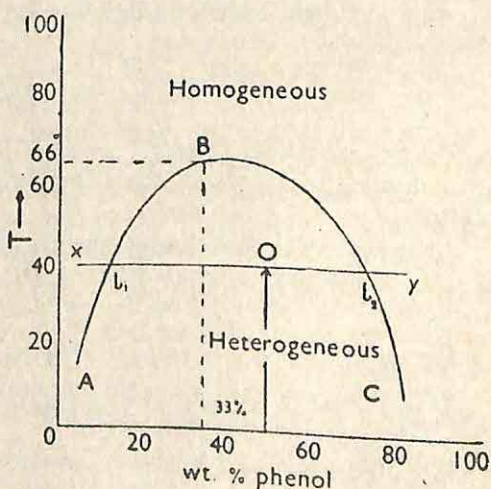


FIG. X.9 Water and phenol (miscibility)

points in AB . AB is thus the boundary between homogeneous and heterogeneous conditions of the system. Similarly at 40°C if we take y percent water in phenol then it would be dissolved fully to produce homogeneous solution. Increased amounts of water, at const. temperature, will lead to the limiting solubility l_2 , beyond which two heterogeneous phases of conjugate solutions would appear. So BC is a boundary on the left of which heterogeneous equilibria would exist and on the right homogeneous. That is, any composition indicated by a point within the area ABC will correspond to heterogeneous phases, whereas any composition indicated by a point outside ABC would lead to the occurrence of homogeneous equilibrium.

Thus at 40°C if a mixture of 50% water and 50% phenol be shaken and allowed to settle, the two conjugate solutions will separate: one layer having composition as at l_1 and the other layer with composition as at l_2 . The relative amounts of the two layers is given by the ratio, ol_2/ol_1 .

These amounts of the conjugate solutions may be easily calculated. For the 50% phenol-water mixture, the compositions of the two liquid layers observed are 9.2% and 65.0% phenol. Let q be the weight of aqueous layer in 100 gms of the mixture and hence $(100-q)$ is the weight of phenolic layer. Evidently

$$q \times \frac{9.2}{100} + (100-q) \frac{65}{100} = 50$$

whence the amount of aqueous layer, $q = 26.8$ gms.

It is also evident that at any temperature above that of B , the two liquids would be miscible in all proportions. This highest temperature above which complete miscibility in all proportions takes place is called *upper consolute temperature* or *critical solution temperature*.

In studying these solubilities, the pressure is always kept constant. There is thus a restriction, i.e., one variable is fixed. Hence, $F = C - P + 1$.

For the homogeneous phase of the two component liquids,

$$F = 2 - 1 + 1 = 2.$$

It would be a bivariant system. So for homogeneous solutions both composition and temperature have to be defined.

For the heterogeneous equilibrium of the two liquids forming conjugate solutions,

$$F = 2 - 2 + 1 = 1$$

i.e., the system would behave as a univariant one. So if either the temperature or the composition be fixed, the other would be automatically known from the diagram.

At the critical solution temperature (B), there is one more additional condition (or restriction) that composition of the two conjugate solutions must be the same.

$$\text{Hence } F = 2 - 2 + 1 - 1 = 0$$

Hence, the point B at the critical solution temperature is a non-variant point.

Many other liquid pairs behave like phenol-water system showing upper consolute temperatures, (Critical solution temp. given in bracket), such as ;

- | | |
|---|---|
| (a) Aniline/hexane ($t = 59.6^\circ\text{C}$) | (d) Cyclohexane/methyl alcohol ($t = 49^\circ\text{C}$) |
| (b) Phenol/isopentane ($t = 63.5^\circ\text{C}$) | (e) Bi/Zinc ($t = 850^\circ\text{C}$) |
| (c) $\text{CS}_2/\text{CH}_3\text{OH}$ ($t = 40.5^\circ\text{C}$) | (f) Aniline/water ($t = 167^\circ\text{C}$) |

X.14. The System : Water and Triethylamine. The t - c diagram of the mutual solubilities of these two liquids is given in Fig. X.10. AB is the solubility curve of triethylamine in water and CB that of water in triethylamine. In both cases, the solubilities decrease with rise in temperature. The two solubility curves become almost horizontal at about 18.5°C and practically merge at this temperature. As in the previous case, any point within ABC corresponds to heterogeneity of the system while outside ABC , the system would be homogeneous. Below the temperature of that of B , the two liquids are miscible in all proportions. The system has thus a lower consolute temperature or critical solution temperature instead of an upper one.

There are other liquid pairs which have lower critical solution temperatures such as : paraldehyde/water ; diethylamine/water, etc.

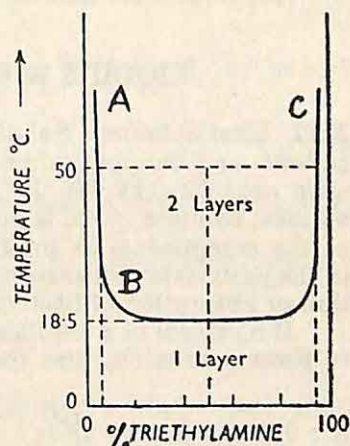


FIG. X.10 Water and Triethylamine (miscibility)

X.15. The system : Water and Nicotine. There are cases where the mutual solubility curve is a closed one having both an upper critical

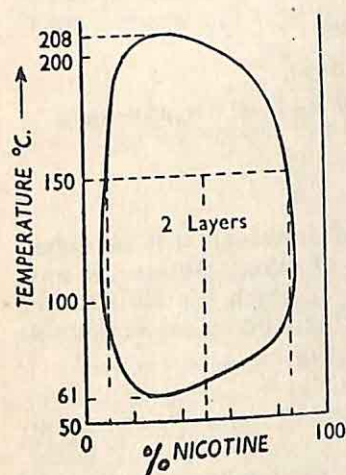


FIG. X.11 Water and Nicotine (miscibility)

solution temperature and a lower critical solution temperature. Such is the system of water and nicotine. The miscibility curves of this pair are represented in Fig. X.11. Above 208°C as also below 61°C , the two liquids are miscible in all proportions. These are the upper and the lower critical solution temperatures. In between these two temperatures with appreciable amounts of the components there would occur heterogeneous phases of two conjugate solutions. Other systems of this type are :

- (a) Methyl ethyl ketone/water ($133^{\circ}/-6^{\circ}\text{C}$)
- (b) Glycerol/*m*-toluidine ($120^{\circ}/7^{\circ}\text{C}$)
- (c) β -picoline/water ($153^{\circ}/49^{\circ}\text{C}$)

X.16. Influence of Foreign Substances on Critical Solution Temperature. The critical solution temperature is very sensitive to the presence of any impurity or foreign substance. The critical solution temperature of phenol-water system

would be raised by 20° if naphthalene be added to make a concentration of only $0.1M$. Again, the critical solution temperature (4°C) of the system acetic acid/cyclo-hexane is raised by about 18° when 1% water is present in the acetic acid. This fact is utilised in ascertaining the presence, and even the amount, of impurities occurring in a sample. For example, petrol and aniline have a known C.S.T. To find out the presence and to estimate the added aromatic hydrocarbons to petrol, C.S.T. is determined with aniline/sample of petrol, and the increase is noted. The amount of impurity is estimated from this increase. Generally critical solution temperature is raised by an impurity if the latter is soluble in one of the liquids only. The C.S.T. is lowered when a third substance present is soluble in both the liquids. The use of soap increases the mutual solubilities of cresols and water and enables us to obtain clear commercial preparations of disinfectant solutions like lysols at ordinary temperatures.

SYSTEMS WITH LIQUID AND VAPOUR PHASES

The equilibria between liquid and vapour phases for two component systems can be conveniently studied if we consider separately the systems in which

imum point (O) will be in equilibrium with a vapour-phase of the same composition; the compositions of the vapour and solution are identical. The diagrams of types II and III are thus made up of two portions: namely (i) one between pure component A and a solution of maximum or minimum vap-pressure and (ii) the other between pure component B and a solution of maximum or minimum vapour pressure.

In type II liquid mixtures having composition between A and O will have vapours richer in B than that in solution *i.e.*, a liquid-composition x will be in equilibrium with vapour-composition x' . But for liquid mixtures having compositions between O and B will have vapours richer in A as compared to that in solution. So a liquid-composition y will be in equilibrium with vapour-composition y' .

Similar findings are also there in type III systems. Liquid mixtures between A and O will have vapours poorer in B than that in solution, as indicated by x and x' . But liquid mixtures between O and B will be richer in B in vapour state than that in solution. Thus, a liquid composition y will be in equilibrium with vapour composition y' .

X.20. Boiling Point-Composition Diagrams. With the variation in composition the vapour pressure of a mixture of two liquids changes. The higher the vapour pressure of a mixture the lower will be its boiling point. Thus, a liquid mixture of type II which has the composition corresponding to maximum vapour pressure will have a minimum boiling point compared to mixtures with any other composition. In other words, if at a fixed pressure, the boiling pt-composition diagrams are prepared, these will be inverted in shape in relation to vapour pressure-composition diagrams. The boiling point-composition diagrams for all the three types of liquid mixtures are shown in Fig. X.19, 22, 23. These diagrams have a direct bearing on the possibility of separating the components of miscible binary liquids. The three types may be considered separately.

(i) **Boiling pt.-Composition Diagram with no Maximum or Minimum.** as in Fig. X.19. ALB is the b. pt.-liquid-composition curve and AKB represents the b. pt.-vapour-composition curve. A liquid mixture, having a composition x will boil at t_1° and the vapour in equilibrium with the liquid will have the composition y ; the b. pt. decreases with increase in conc. of B . If this vapour be removed and condensed the liquid will have the same composition y . If this condensed liquid be boiled again, it will boil at t_2° and the vapour in eqm. will have composition z .

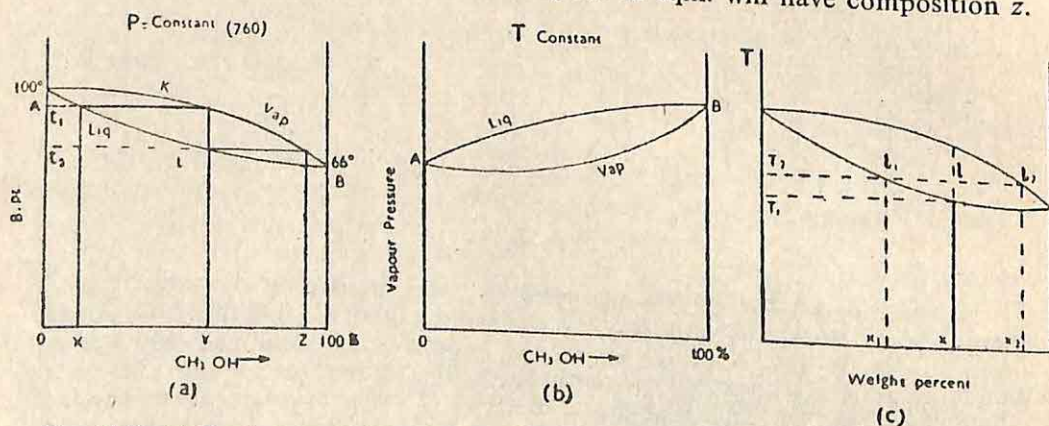


FIG. X.19. (a) B. pt.-composition diagram (b) Vap-Pr.-composition diagram (Type I system) H_2O/CH_3OH (c) Ratio of distillate to residue on distillation

On removing this vapour and condensing, a liquid of composition z will be obtained. On repeating this process of boiling and condensing in successive fractions, ultimately the pure component B would be obtained. In the residual liquids the component A would gradually be increasing. The two liquids can thus be separated from such a mixture of type I. The tedious process of successive evaporation and condensation is in practice avoided by using a fractionating column in distillation.

Fractional distillation. A common fractionating column used in laboratory is a fairly long glass tube fitted vertically above the distilling flask and packed with glass beads (Fig. X.20). When the liquid mixture boils, the vapour rises up in the column and progressively cools as it goes higher

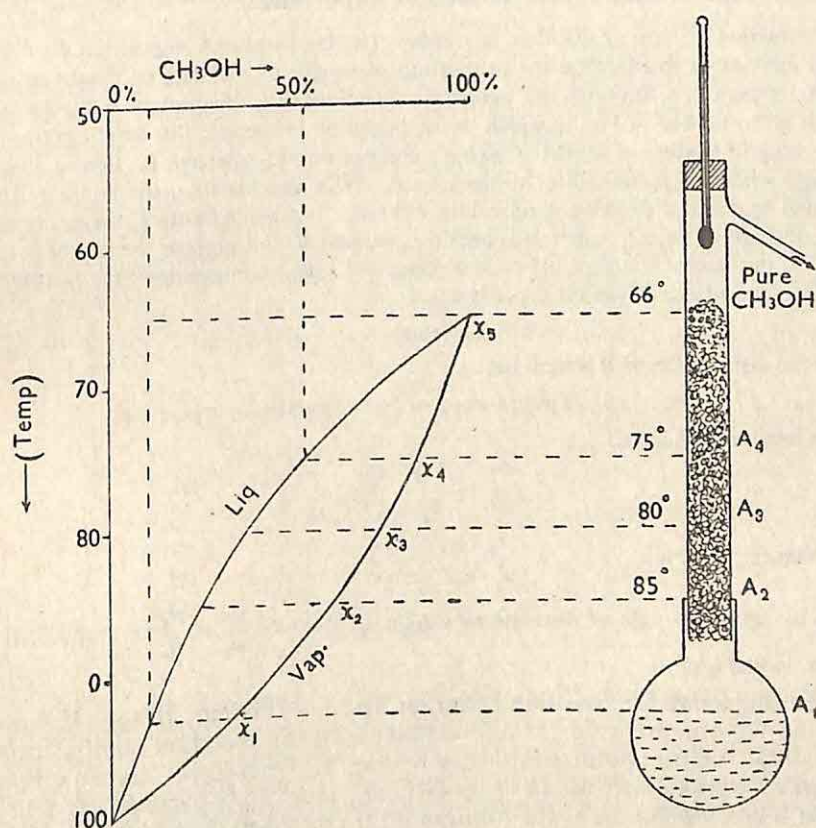


FIG. X.20 Representation of fractional distillation in a column

and higher. Suppose we start with $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ mixture in the flask having about 10% methylal. It would boil at about 92°C , the vapour having the composition x_1 . When this vapour goes up in the column, at the point A_2 a portion will condense and the vapour (say at 85°C) will have the composition x_2 . As more hot vapour goes up, this condensate is obtained boils and at the point A_3 (relatively cooler) a condensate is obtained (say at 80°C) in eqm. with a vapour having composition x_3 . In its turn this liquid will also boil when higher temperature vapours come up from below producing vapours richer in CH_3OH . Ultimately the point A_5 is reached when the temperature is 66° or less, the condensate will be in equilibrium with pure CH_3OH , which is easily separated. An upward flow of the vapour and opposite downward flow of the liquid helps the separation. The efficiency is increased if the process is carried out slowly and large surface areas are allowed for attaining equilibria at different points by using glass beads etc. In a large scale fractionation, instead of a column a tower is used which is divided into a number of compartments by plates set one above the other. These plates have central openings covered by loose bubble caps which allow the vapour to go up. The condensed liquid drops down by overflow pipes as in Fig. X.21. The principle of separation is the same.

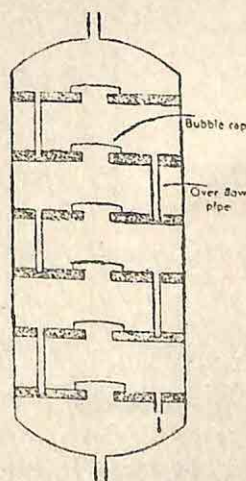


FIG. X.21
Fractionating tower

Complete separation of the two liquids by fractional distillation is possible only in type I mixtures where the vap-pressure progressively changes from that of one component to that of the other component. Liquid air being such a mixture, it is possible to obtain pure oxygen and pure nitrogen from the same by fractional distillation. This has enormous industrial importance.

Determination of ratio of distillate to residue. The temperature-composition distillation diagram also enables us to calculate the proportion of weight of distillate to weight of residue at any given temperature. Suppose the temperature-composition diagram of a binary system of *A* and *B* is given by Fig. X.19c, in which the composition is expressed in weight percent. Let us start with a liquid mixture of weight *w* having a composition of *x* percent *B*. The liquid will begin to boil only when the temperature is raised to *T*₁. With vaporisation, the liquid will be more concentrated in *A* and the boiling temperature will rise. At a temperature *T*₂ (say), the liquid will have the composition as at *l*₁ which will contain *x*₁ percent *B*, and suppose the weight of the liquid now is *w*₁. If the system is closed, the vapour phase will have a composition as at *l*₂, containing *x*₂ percent of *B*; the weight of vapour phase is *w*₂. Thus

$$w_1 + w_2 = w$$

And from the distribution of *B* is such that

$$wx = w_1x_1 + w_2x_2; \text{ i.e., } (w_1 + w_2)x = w_1x_1 + w_2x_2$$

from these relations, we have,

$$\frac{w_1}{w_2} = \frac{(x_2 - x)}{x - x_1}$$

from the diagram, we find,

$$\frac{x_2 - x}{x - x_1} = \frac{ll_2}{ll_1}$$

Hence the ratio of weight of distillate to weight of residue, $\frac{w_2}{w_1} = \frac{ll_1}{ll_2}$, i.e., ratio of the intercepts of the tie-line *l*₁*l*₂.

(ii) Boiling point-Composition Diagram with a Minimum. In type II liquid pair systems, the vapour pressure reaches a maximum for a certain composition. The corresponding boiling point-composition diagram therefore shows a minimum at the same composition as in Fig. X.22(a) [for H₂O/pyridine system]. If a mixture with a composition at the minimum (*M*) be taken, it would boil at a fixed temperature and the vapour will have the same composition as the liquid.

Such a mixture which possesses a higher vapour pressure or a lower vapour pressure than any other mixture is called an *azeotropic mixture*. Evidently, the azeotropic mixture will have a boiling point higher or a boiling point lower than any other mixture. The azeotropic mixture distils unchanged in composition and hence these are termed *constant boiling mixtures*.

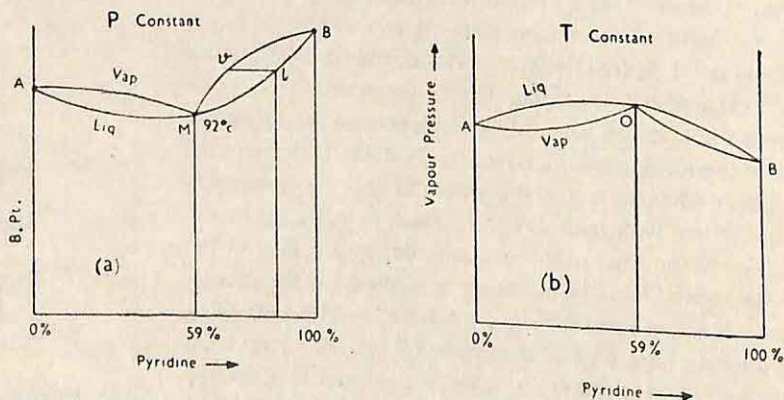


FIG. X.22(a) B. pt.-composition diagram (b) Vap-pressure-composition diagram for Type II system (H₂O/Pyridine).

The type II water-pyridine system has a maximum vap-pressure and a minimum b. pt. 92°C at a composition of 59% pyridine, [Fig. X.22]. If we distil a water-pyridine mixture having a composition (say *l*) in which pyridine is more

than 59%, the distillate will be poorer in pyridine and the residual liquid will be richer in pyridine. By repeating the process, (as in type I) we can separate pure pyridine in the flask and the azeotropic mixture in the distillate. On the other hand, if a mixture containing less than 59% pyridine be distilled, the distillate will be richer in pyridine and the liquid in the flask will be richer in water. Ultimately by repetition of the process here we can obtain pure water and the azeotropic mixture. In other words, by fractional distillation, any mixture of type II can be separated only to one pure component and the azeotropic mixture. It is not possible to separate them into two pure components by distillation. If the mixture has the azeotropic composition, it will distil unchanged.

Similar behaviour is also found in water-ethyl alcohol mixture. The azeotropic mixture has the minimum b. pt. 78.2° with 95.6% alcohol. When a dilute alcoholic solution is fractionally distilled it separates into pure water and the azeotrope (95.6% alcohol). When a conc. alcohol solution is fractionally distilled we obtain pure ethyl alcohol and the azeotrope. Complete separation of alcohol is not possible. The rectified spirit sold in the market is the azeotropic mixture (95.6%). Some other liquid pairs having minimum b. pt. mixtures are listed below.

BINARY MIXTURES TYPE II (minimum b. pt.)

Components		Min. b. pt.	Composition
A	B	(°C)	% of B
H ₂ O	ethyl alcohol	78.1	95.6
H ₂ O	n-propyl alcohol	88	72
C ₆ H ₆	acetic acid	80.05	2
H ₂ O	pyridine	92.6	59
CS ₂	ethyl acetate	46	3

(iii) **Boiling pt.-Composition Diagram with a Maximum.** In type III liquid pair system, the vapour pressure-composition diagram shows a minimum. Consequently, the b. pt.-composition diagram would show a maximum. That is, at a certain composition [at M in Fig. X.23(a),] there is an azeotropic mixture boiling at a fixed temperature unchanged in composition. Such a system may be illustrated with H₂O/HNO₃ mixture.

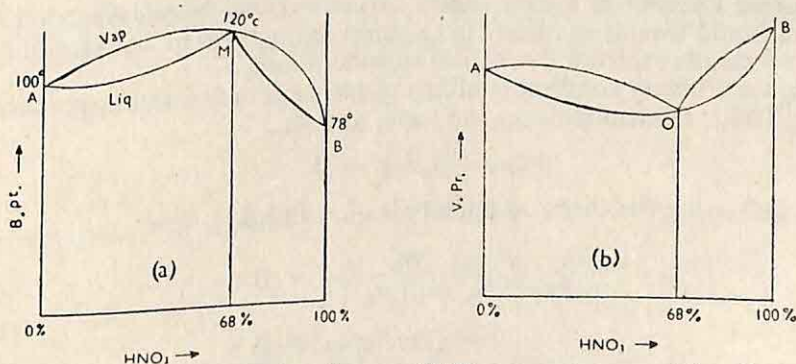


FIG. X.23 (a) B. pt.-composition diagram (b) Vap.-pressure-composition diagram in Type III system (H₂O/HNO₃)

As in type II systems, it is easily seen that if a dilute solution of HNO₃ be distilled, it is possible to separate it into pure water and an azeotrope (68% HNO₃, b. pt. 120°C). When the azeotropic composition is reached, the liquid will distil unchanged. A higher concentration of HNO₃ cannot be obtained by distillation. On the other hand, if a conc. solution of HNO₃ be distilled, we can separate it into pure HNO₃ and the azeotropic mixture. Complete separation of HNO₃ by distillation is not possible.

Other binary mixtures with maximum constant boiling point are :

BINARY MIXTURES TYPE III (maximum b. pt.)

Components		Max. b. pt. °C	Composition % of B
A	B		
H ₂ O	HNO ₃	120.5	68.0
H ₂ O	HCl	108.5	20.2
H ₂ O	HBr	126	47.5
H ₂ O	HI	127	57.0
H ₂ O	HCOOH	107	77.0
CHCl ₃	CH ₃ COCH ₃	64.7	20.0

Azeotropic Mixtures. In applying phase rule to azeotropic mixtures, we should remember that there is one restriction, namely, the compositions in liquid and in vapour phase are the same. Hence

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

i.e., azeotropes should behave as univariant system, so that the boiling point will be constant if pressure is fixed. This is what we have already seen.

The fact that azeotropes boil at a definite temperature and the liquid and vapour have identical composition, suggests that these may be true chemical compound. But this is not so, because (i) the composition of constant boiling mixtures depends upon the pressure, (ii) the composition does not correspond to any stoichiometric proportion of the components, (iii) there is no spectroscopic evidence of the formation of a compound between the components.

The separation of the components in an azeotropic mixture is rendered possible usually by one of the following methods. (i) By distillation with a third substance, e.g., absolute alcohol can be recovered by distilling rectified spirit (azeotrope) with benzene. (ii) By chemical reactions, e.g., nitration will remove aromatic components from a mixture with saturated hydrocarbons, or lime may be employed in removing water from rectified spirit. (iii) by adsorption, e.g., charcoal or silica gel may be used to adsorb one of the components. (iv) By solvent extraction, one component may be extracted by adding a suitable immiscible solvent.

X.21. Vapour Pressure of Binary Liquid Mixtures from Thermodynamic Considerations. The liquid vapour equilibria in mixtures as observed in the preceding sections are also substantiated from theoretical considerations.

Suppose a binary solution contains n_1 gm-moles of A and n_2 gm-moles of B. Applying Gibbs-Duhem relation, we have, at eqm.,

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

where μ_1 and μ_2 are the chemical potentials of A and B.

$$\therefore \frac{n_1}{n_1 + n_2} d\mu_1 + \frac{n_2}{n_1 + n_2} d\mu_2 = 0$$

$$\text{i.e., } N_1 d\mu_1 + N_2 d\mu_2 = 0$$

... (X.24)

where N_1 and N_2 are the mol-fractions.

When the liquid mixture of A and B is in equilibrium with their vapour phase at const. temperature T , the chemical potentials will be the same in both the phases for each component, Since

$$\mu_i = RT \ln f_i + z_i \quad (f_i, \text{ fugacity})$$

or assuming the vapours behaving ideally, we can write, $\mu_i = RT \ln P_i + z_i$ where P_i is the partial pressure of the i -th component in the vapour phase.

That is,

$$d\mu_i = RT d \ln P_i$$

Substituting in eqn. (X.24),

$$N_1 RT d \ln P_1 + N_2 RT d \ln P_2 = 0$$

$$\text{or} \quad \frac{N_1 d \ln P_1}{dN_1} + \frac{N_2 d \ln P_2}{dN_1} = 0$$

$$\text{Since} \quad N_1 + N_2 = 1, \quad dN_1 = -dN_2,$$

$$\therefore \quad \frac{N_1 d \ln P_1}{dN_1} - \frac{N_2 d \ln P_2}{dN_2} = 0$$

$$\text{or} \quad \frac{d \ln P_1}{d \ln N_1} = \frac{d \ln P_2}{d \ln N_2} \quad \dots \text{ (X.25)}$$

This equation, called **Duhem-Margules equation**, is indeed a correlation between the composition in the liquid phase and the partial vapour pressures in the gas-phase.

Now, if we consider an ideal solution, Raoult's law is applicable, i.e.,

$$P_1 = P_1^0 N_1$$

$$\text{or} \quad d \ln P_1 = d \ln N_1, \quad \text{i.e.,} \quad \frac{d \ln P_1}{d \ln N_1} = 1$$

$$\text{Since from eqn. (X.25),} \quad \frac{d \ln P_2}{d \ln N_2} = \frac{d \ln P_1}{d \ln N_1}$$

$$\therefore \quad \frac{d \ln P_2}{d \ln N_2} = 1$$

Hence, for a solution in which component 1 obeys Raoult's law at all compositions, the other component 2 will also obey it.

$$\text{That is,} \quad P_2 = P_2^0 N_2$$

The partial pressures will bear a linear relationship through the entire composition to the mol-fractions of the components. This we have seen to be true in section X.18. The total vapour pressure will also change linearly with composition as in equation X.22 (Fig. X.12). As already pointed out such ideal solutions are rare. In real or non-ideal solutions, there is departure from Raoult's law; the vapour pressure of a component in the mixture is either greater or less.

(i) When the deviation is positive, $P_1 > P_1^0 N_1$.

$$\therefore \quad \frac{d \ln P_1}{d \ln N_1} > 1$$

But for any solution, from Duhem-Margules relation

$$\frac{d \ln P_1}{d \ln N_1} = \frac{d \ln P_2}{d \ln N_2}$$

$$\text{Hence} \quad \frac{d \ln P_2}{d \ln N_2} > 1, \quad \text{or} \quad P_2 > P_2^0 N_2$$

Or, if there is a positive deviation for one component, the second component must also exhibit positive deviation. This has actually been observed (Fig. X.16).

(ii) When the deviation is negative, $P_1 < P_1^0 N_1$

$$\text{Hence} \quad \frac{d \ln P_1}{d \ln N_1} < 1$$

$$\text{As before} \quad \frac{d \ln P_2}{d \ln N_2} < 1, \quad \text{or} \quad P_2 < P_2^0 N_2$$

Or, when one component in the solution shows negative deviation from Raoult's law, the other component would also exhibit the same. This has actually been realised (Fig. X.17).

It can also be shown thermodynamically that positive deviations are found in cases where solutions are formed with absorption of heat, whereas negative deviations occur in cases where solutions are formed with evolution of heat.¹

It is also possible to predict the effect of alteration in composition of the liquid on the total vapour pressure of the system. Suppose in the liquid phase the mol-fractions of the two components are N_1 and N_2 , and the mol-fractions in the vapour-phase N_1' and N_2' . The total vapour pressure, $P = P_1 + P_2$.

$$\begin{aligned} \text{We have} \quad & \frac{d \ln P_1}{d \ln N_1} = \frac{d \ln P_2}{d \ln N_2} \\ \text{i.e.,} \quad & \frac{N_1 dP_1}{P_1 dN_1} = \frac{N_2 dP_2}{P_2 dN_2} \end{aligned} \quad \dots (X.26)$$

$$\text{or} \quad \frac{dP_1}{dN_1} = \frac{N_2 P_1}{N_1 P_2} \cdot \frac{dP_2}{dN_2}$$

$$\text{Now} \quad P = P_1 + P_2$$

$$\text{or} \quad \frac{dP}{dN_1} = \frac{dP_1}{dN_1} + \frac{dP_2}{dN_1} = \frac{N_2 P_1}{N_1 P_2} \cdot \frac{dP_2}{dN_2} - \frac{dP_2}{dN_2} \quad (\text{since } dN_1 = -dN_2)$$

$$\text{or} \quad \frac{dP}{dN_1} = \frac{dP_2}{dN_2} \left[\frac{N_2 P_1}{N_1 P_2} - 1 \right] \quad \dots (X.27)$$

Assuming that vapours behave ideally (though the solution may not be so), we can say,

$$\begin{aligned} \frac{P_1}{P_2} &= \frac{N_1'}{N_2'} \\ \therefore \quad \frac{dP}{dN_1} &= \frac{dP_2}{dN_2} \left(\frac{N_2}{N_1} \cdot \frac{N_1'}{N_2'} - 1 \right) \end{aligned} \quad \dots (X.28)$$

Now $\frac{dP_2}{dN_2}$ is always positive, hence

$$\frac{dP}{dN_1} \text{ is positive, when } \frac{N_2}{N_1} \cdot \frac{N_1'}{N_2'} > 1, \text{ or } \frac{N_1'}{N_2'} > \frac{N_1}{N_2}$$

This means that total vapour pressure (P) will increase with the increase in the mol-fraction of the component which is present relatively in higher proportion in the gas-phase than in the liquid phase. ... (A)

$$\text{Again,} \quad \frac{dP}{dN_1} \text{ is negative, if } \frac{N_1'}{N_2'} < \frac{N_1}{N_2}$$

That is, the addition of a component which is relatively less in gas-phase than in liquid phase will lower the total vapour pressure. ... (B)

These conclusions (A) and (B) had been embodied empirically by Konowaloff in a general principle from experimental observations. The principle is often mentioned as **Konowaloff's Rule**.

In type II and type III systems there is a maximum or minimum in the vapour-pressure curves and at such points $\frac{dP}{dN_1}$ must be zero. From equation (X.28), we find that for maximum or minimum points,

$$\begin{aligned} \frac{N_2}{N_1} \cdot \frac{N_1'}{N_2'} &= 1 \\ \text{i.e.,} \quad \frac{N_1'}{N_2'} &= \frac{N_1}{N_2} \end{aligned}$$

So, for a maximum or minimum, i.e., for azeotropes, the composition in the vapour phase is the same as that of the liquid with which it is in equilibrium.

¹See "Thermodynamics" by the author, Chapter 12.

LIQUIDS WHICH ARE PARTIALLY MISCIBLE

X.22. Vapour Pressure and Distillation Diagrams for Partially Miscible Liquids. If two partially miscible liquids are brought together homogeneous liquid mixture will result only when the proportion of either component is small. But when the proportions of the components are high, two liquid phases of conjugate solutions will appear. Since each liquid depresses the vapour pressure of the other, the vapour pressure of the conjugate solution is less than the sum of the vapour pressures of the two pure components.

A vapour-pressure-composition diagram for the liquid pair amyl alcohol/water is given in Fig X.24(a). The vapour pressures of pure amyl alcohol and pure water are A' and B' . As water is slowly added to amyl alcohol, first homogeneous solution is formed. The total vapour pressure increases along $A'C'$. At C' amyl alcohol is saturated with water and on further addition of water a separate layer will begin to form. Similarly if amyl alcohol is added to water, the total vapour pressure

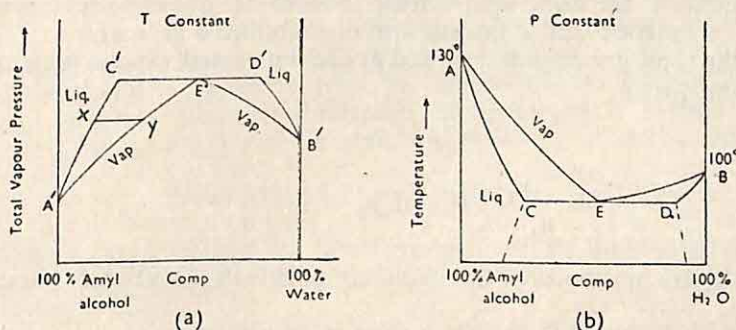


FIG. X.24 (a) Vap-pressure-comp. diagram (b) B. pt. comp. diagram for partially miscible liquid pair, amyl alcohol/water.

will change along $B'D'$ and at D' a saturated solution of amyl alcohol in water is formed and two layers will occur on further addition of amyl alcohol. Between the points B' and D' , for all compositions there shall be two layers of conjugate solution. The total vapour pressure over the conjugate solutions between the points C' and D' remains constant, as indicated by the horizontal portion $C'D'$. This vapour pressure is the vapour pressure of either of the two layers. This is anticipated from the Phase Rule. Between C' and D' , there are three phases, hence

$$F = 2 - 3 + 2 = 1,$$

the system becomes univariant. So, if temperature is fixed, the vapour pressure and the composition of both vapour phase and the distillate will be fixed. The curves $A'E'$ and $B'E'$ show the change in vapour compositions (with changes in pressure) in eqm. with $A'C'$ and $B'D'$. For all liquid composition between C' and D' , the composition of the vapour is constant and is equal to that at E' .

The corresponding b. pt.-composition diagram is given in Fig. X.24(b). A and B are the boiling pts. of pure components—amyl alcohol and water. AC represents the change in boiling pt. of homogeneous solution of water in amyl alcohol, and BD that of amyl alcohol in water. Between the points C and D , two separate layers exist. Along CD the system is univariant, hence for a given pressure (say 1 atmosphere), the boiling point will be fixed. AE and BE denote the vapour composition in equilibrium with AC and BD . The point E denotes the composition of the vapour produced by boiling any two-layer mixture between C and D . In this system of amyl alcohol/water, the constant boiling point of CD is about 95°C (under 1 atmosphere) which is lower than that of either amyl alcohol or water. When a two-layered system is distilled, the amounts in the liquid phases will gradually decrease, and generally, one of the phases will disappear before the other one, depending on the initial relative amounts of the two layers. If the phase C disappears first, then further progress of distillation will proceed along DB and EB , and ultimately

boiling temp. will reach 100°C and pure water will distil. On the other hand if phase D disappears earlier, the curves CA and EA will represent distillation and finally pure amyl alcohol will be obtained (b. pt. $= 130^{\circ}\text{C}$).

Similar behaviour is noticed in other systems like $\text{CH}_3\text{OH}/\text{CS}_2$, water/butyl alcohol, aniline/water, ethyl acetate/water, etc. The distillation diagram varies somewhat when the constant boiling point of conjugate layers is in between the boiling temperatures of pure components.

IMMISCIBLE LIQUID PAIRS

X.23. Vapour Pressure and Distillation of Immiscible Liquids. Immiscible liquids are mutually insoluble. When such liquids are brought together, each liquid behaves independently of the other. Consequently, the vapour pressure of a mixture of two immiscible liquids at any temp. is the sum of the vapour pressures of the individual pure components at the same temperature. Moreover, the vap-pressure above the mixture will be independent of the amount of each liquid present.

If P be the total pressure and p_1 and p_2 are the partial vapour pressures of the two components, then

$$P = p_1 + p_2$$

further

$$p_1 = \frac{n_1}{n_1 + n_2} P \text{ and } p_2 = \frac{n_2}{n_1 + n_2} P$$

where n_1 and n_2 are gm-moles of the two components in the vapour phase, in any given volume.

$$\therefore p_1/p_2 = n_1/n_2$$

Since at a given temperature p_1/p_2 is constant, so n_1/n_2 is also fixed. That is, the vapour-composition is always the same, as long as both liquids are present. If weights of the components in the vapour-phase (i.e., the distillate) be w_1 and w_2 , then

$$\frac{p_1}{p_2} = \frac{w_1/M_1}{w_2/M_2} \quad (M_1, M_2 \text{ are mol. wts.})$$

or

$$\frac{w_1}{w_2} = \frac{p_1 M_1}{p_2 M_2} \quad \dots (X.29)$$

The weights of two components in the distillate depend on the mol. wts. and vapour pressures of the two pure components. We shall presently see that this relation is taken advantage of in steam distillation.

As the temperature is raised, the vapour pressure of each liquid will increase, so that total vapour pressure will rise. When this total vapour pressure is equal to the external pressure, the mixture will boil and distillation goes on with a constant composition of the distillate. The boiling point will be lower than the boiling point of either of the two liquids.

Steam distillation. When a liquid (or a solid) X , which is immiscible with water, is to be separated from other non-volatile impurities, it is often distilled with steam. The process becomes particularly useful when the substance X is high-boiling and decomposes near its normal boiling point. In steam distillation, the substance is distilled with steam at a temperature considerably below (near about 100°C) its normal boiling point and the danger of decomposition is avoided. To illustrate : iodobenzene (b. pt. 188°C) is purified by steam distillation at about 98°C . At this temperature, $p_{\text{H}_2\text{O}} = 712 \text{ mm}$ and $p_{\text{iodobenzene}} = 48 \text{ mm}$, so that total pressure $= 760 \text{ mm}$.

The liquid to be purified is taken in a flask mixed with water and heated. Steam from a separate generator is also simultaneously injected. When the temperature is raised high enough to make $p_1 + p_2 = 760 \text{ mm}$, the mixture distils with a composition given by equation X.29.

In the case of iodobenzene mentioned above,

$$\frac{w_1}{w_2} = \frac{M_1 p_1}{M_2 p_2} = \frac{204 \times 48}{18 \times 712} \approx \frac{7}{9} \text{ (approx.)}$$

Hence, out of every 16 gms of distillate, 7 gms would be iodobenzene. Though the vapour pressure of iodobenzene is much lower, but its high molecular weight counterbalances so as to make the relative yield appreciably large.

It is easily seen that approximate mol. wt. of a substance X can also be obtained from the equation (X.29), provided the vapour pressures are known.

SOLID-LIQUID PHASES

X.24. Solid-Liquid Equilibria. In solid-liquid binary systems it is important to follow the crystallisation or melting processes. In considering the equilibria in solid-liquid systems, or condensed systems as they are often called, the vapour phase is regarded as absent. Small variations in pressure have little effect on such equilibria, and moreover, studies on such equilibria are usually carried out at constant external pressure, generally the atmospheric pressure. The phase rule then, with the restriction of constancy of pressure, takes the form

$$F = C - P + 1 = 2 - P + 1 = 3 - P$$

The variables in such systems are therefore temperature and composition. That is why temperature-composition diagrams are best suited to represent the equilibria of solid-liquid systems.

To determine the equilibrium in such a system, it is necessary to find out the amounts or concentrations of either of the components in solid and in liquid phases at different temperatures. Two methods are most commonly employed to obtain this information : (i) thermal analysis and (ii) solubility measurements.

(i) **Thermal Analysis.** This method is employed where solids crystallise out from the molten mixture of the components, such as crystallisation of lead from the molten Pb-Sn alloy. The solids separating out may be pure components, their compounds or solid solutions. In this method, the cooling-rates during the process of solidification of various compositions of the system are followed *i.e.*, time-temperature diagrams during the process are prepared. From these diagrams, the temperature at which transition occurs can be obtained, as also the temperatures at which crystallisation from the molten mass begins and ends are known.

When a pure substance (A) in the molten state is cooled slowly the time-temperature curve will have the form as shown in Fig. X.25(a). In this diagram pq denotes the rate of cooling of the molten liquid. At q the freezing pt. is reached and the liquid begins to solidify ; the temperature remains constant until the whole liquid becomes solid as shown by horizontal line qr . Thereafter the portion rs indicates the progressive cooling of the solid.

But when a molten liquid of two components (A and B) or a solution is cooled slowly, the cooling curve is different as in Fig. X.25(b). The portion pq as before represents the cooling of the molten liquid (or solution). At q one of the components begins to crystallise out slowly. The system has now two phases, *i.e.*, ($F = 3 - 2 = 1$), the system becomes univariant. With crystallisation, the composition of the liquid mixture changes slowly, so the eqm. temperature must also change. Due to change in the rate of cooling there is a break in the cooling curve at q called the initial "arrest". Such a state continues until the point o is reached when the other component (or it may be a compound of the two) also begins to solidify. There are now three phases, two solids and a liquid, hence $F = 3 - P = 0$. Hence one of the phases must disappear before further change in temp. *i.e.*, the entire liquid will now solidify at a constant temperature represented in the curve by or . The point o registers a second break, called the final "arrest". The portion rs indicates the progressive cooling of the solidified mass. The temperature

variation is recorded with a sensitive thermometer or a standardised thermocouple. The temperature at the arrest points for any mixture of given composition can be ascertained with good precision.

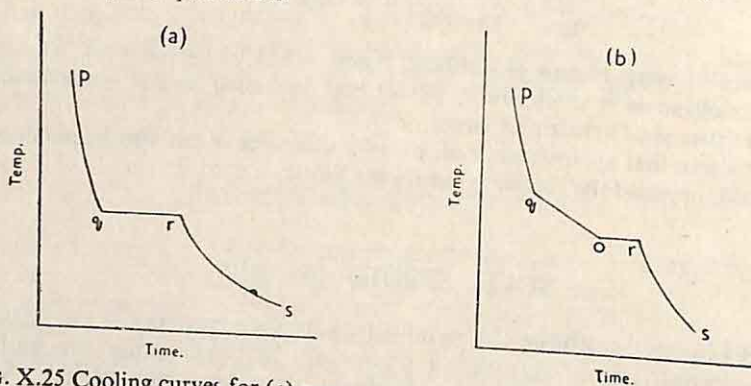


FIG. X.25 Cooling curves for (a) pure component, (b) solution of two components.

To construct the phase diagram, a number of mixtures of *A* and *B* are taken with different proportions, preferably equally spaced from 100% *A* to 100% *B*. Each of these mixtures are heated to their molten states and then cooling curves are obtained separately for each mixture. A set of such cooling curves are shown in Fig. X.26(a). If the initial arrests (*q*) of different mixtures are joined, a curve AOB is obtained as shown in Fig. X.26(b). Any point on this line indicates the

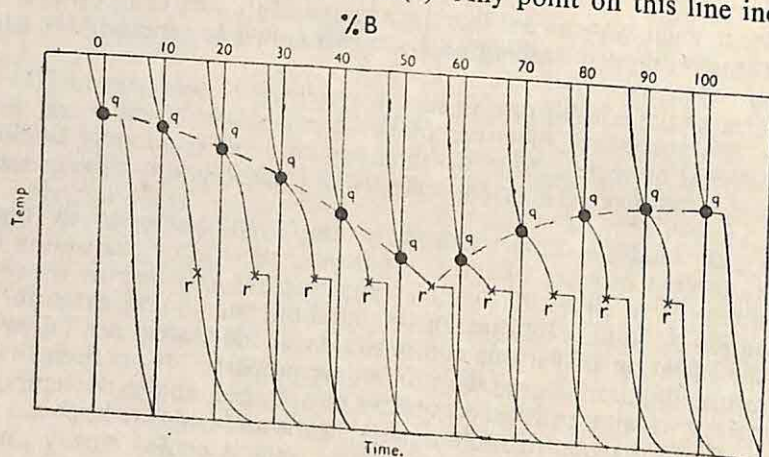


FIG. X.26(a)

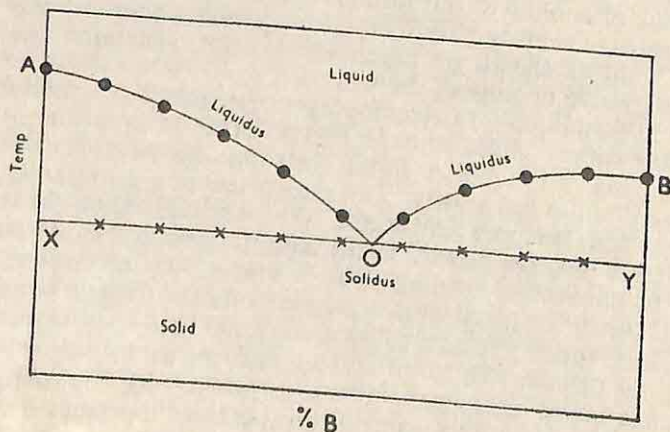


FIG. X.26(b)

appearance of a solid phase from the liquid. This curve is named "*liquidus*". The area above this curve represents the system in liquid phase only. Again, by joining the final arrests (*r*-points) of the different cooling curves, a horizontal line XOY is obtained when every mixture solidifies in entirety. AXOYB is called the "*solidus*." Below this line, no liquid phase would exist. In between the liquidus and solidus in the areas AXO and BYO, one of the components in solid state will be in equilibrium with liquid mixture. The point O, called the *eutectic point*, is characterised by the fact that the three phases would co-exist at this point.

(ii) *Solubility measurements*. This method is successfully employed where one of the components remains in liquid state and the other in solid state for a considerable range of temperature, such as the equilibria of salts and their aqueous solutions. In fact, this method is extensively used in the study of equilibria of salt hydrates. The determination of solubility of a salt at a given temperature gives the amount of the salt component in solution which may remain in equilibrium with its solid phase. Measurements of saturation limits at different temperatures lead to the phase diagram. On the other hand if very dilute solutions are used, these are cooled sufficiently below 0°C, when ice would separate out. It is thus possible to find out the equilibria of solid ice with solution from the freezing point curve. Illustrations of this method will be found in the subsequent sections.

TWO COMPONENT SOLID-LIQUID PHASES

The two component solid-liquid systems are divided into several types based on miscibility in their liquid state and on the nature of the solids separating from the solution. The components are completely miscible in liquid phase.

Type I Pure components crystallise from the solution.

Type II Solid compound of the components with congruent m.pt. separates from the solution.

Type III Solid compound of the components with incongruent m.pt. separates from the solution.

Type IV The solids crystallising are solid solutions which are completely miscible.

Type V The solids crystallising are solid solutions which are partially miscible.

These may now be illustrated with some familiar examples :

X.25. Simple Eutectic Systems. The Fig. X.27 represents the phase diagram of such a eutectic system in which the two components *A* and *B* are completely miscible in liquid state and pure components only crystallise from solution. In this diagram *A* and *B* are the freezing points of pure components *A* and *B*. The addition of component *B* to *A* will cause the temperature of equilibrium or freezing point to be lowered. The points on AE denotes the concentrations of solutions saturated with *A* at different temperatures between *A* and T_B , i.e., AE is the freezing points of solutions which yield *A* as a solid phase. Similarly the curve BE denotes the freezing points of solutions which yield *B* as a solid phase from the solutions (between the temperatures T_B and T_E). At E, the point of intersection of the two curves, the solution is saturated with both *A* and *B*. Hence at E, three phases co-exist, namely, solution, solid *A* and solid *B*.

Therefore at E, $F = C - P + 1 = 2 - 3 + 1 = 0$, the system is non-variant. Both temperature and composition are fixed. This means if either the temperature or the composition is altered, one of the phases will disappear. If the temperature is lowered, the saturated solution will disappear and the whole mass will solidify as a mixture of pure *A* and pure *B* crystals. If the temperature is raised, the solids will melt. The temperature at E, i.e., T_E is the lowest temperature at which a liquid phase may exist in the system. The point E is called the *eutectic point*, the composition L is the *eutectic composition* and T_E the *eutectic temperature* of the system. The eutectic mixture has a definite composition (L) and definite melting

point (T_E), yet it is not to be regarded as a compound for, (i) the components are not in stoichiometric proportion and (ii) the mixtures reveal the existence of separate crystals under a microscope.

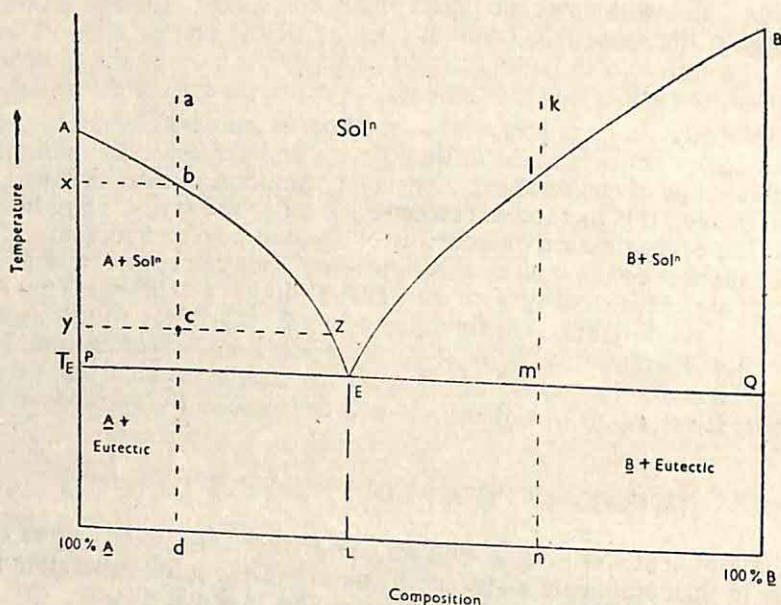


FIG. X.27 Simple eutectic diagram

Along the line AE, crystals of *A* separate from the solution. The points on this line indicate the "beginning of freezing" and is the *liquidus*. Likewise the line BE is the other *liquidus* which represents the beginning of freezing of *B* from the solution. The system has thus the *liquidus* AE and BE. The end of freezing or the beginning of melting of different composition of the system is given by the line PEQ. This line along with AP and BQ forms the *solidus*. Between the *solidus* and the *liquidus*, there are two phases, one solid and the liquid in eqm. Hence the system would be monovariant, i.e., for a given temperature composition is fixed. In the region APE we have solid *A* and solution and in the region BQE there are solid *B* and solution, in equilibrium.

Above the lines AE and BE, the region represents the unsaturated solution. Since there is only one solution phase, the system becomes bivariant. In order to define a system in this area, both the temperature and composition have to be specified. The practical meaning of these curves and areas can be easily understood by considering the behaviour of a given mixture on cooling.

Suppose a mixture with composition (*d*) is taken and heated sufficiently as to give a homogeneous solution represented by point *a*. This liquid may now be slowly cooled. When the temperature will come down to the point *b* on the *liquidus*, crystals of *A* will begin to separate and will be in equilibrium with a solution saturated with *A* and the temperature is *X*. On further cooling, more and more crystals of *A* would separate. The proportion of *B* in the solution will increase. In other words, with progressive cooling the composition of the saturated solution will change along the curve BE. Thus when the system cools down to the point *c*, the temperature is *y* and the composition of the liquid phase corresponds to *z*. When the temperature T_E (that of the eutectic) is reached, the other solid *B* also crystallises. The liquid will have the composition as at *E*, i.e., *L*. At this constant temperature (T_E) the whole liquid will tend to solidify. The liquid phase will be non-existent below this temperature, and a mixture of *A*-crystals and eutectic solid mixture of *A* and *B* will be formed.

Similar behaviour is also observed if a liquid phase of composition *k* be slowly cooled. At the point *l*, the solid phase *B* will separate in eqm. with its saturated

solution, whose composition moves along IE . The entire mass will solidify at temperature T_E , giving B -crystals and eutectic mixtures of A and B solids.

The proportions of a solid in eqm. with the liquid phase can also be determined from the diagram. Suppose the system of composition ' a ' is at a temperature γ . The system will then have pure A crystals in eqm. with solution having composition z . The amount of solid separated is proportional to cz and the amount of saturated solution present in eqm. is cy (of composition z). The ratio of their amounts is $cz : cy$. From this ratio and the total weight, it is possible to estimate the expected yield of a solid at a given temperature. We may now take some specific examples of simple eutectic system.

The system Sb-Pb. The two component system of antimony and lead is an example of simple eutectic type, the phase diagram is given in Fig. X.28. The melting pt. of pure antimony is 631°C and of pure lead 327°C . With increasing amounts of lead added to antimony, the freezing pt. of the latter is lowered along AE . Likewise BE is the freezing pt. curve of lead with added quantities of antimony. AE and BE form the liquidus of the system. E is the eutectic point (temp. 246°C and composition 87% Pb). $ADEFB$ is the solidus.

Above AEB , the system is one liquid phase only, hence bivariant. Between temperature limits A and D , and composition range D and E , i.e., in the area AED , solid antimony is in equilibrium with solution phase. In the area BEF , solid lead is in equilibrium with solution phase. Below eutectic temp. $T_e = 246^\circ\text{C}$, the system will be composed of solid phases of crystals of lead and antimony. If the system has just the eutectic composition (87% lead), it will sharply melt at E ($T_e = 246^\circ\text{C}$) to form the liquid phase of the same composition. At E , solid lead, solid antimony and the solution phase coexist.

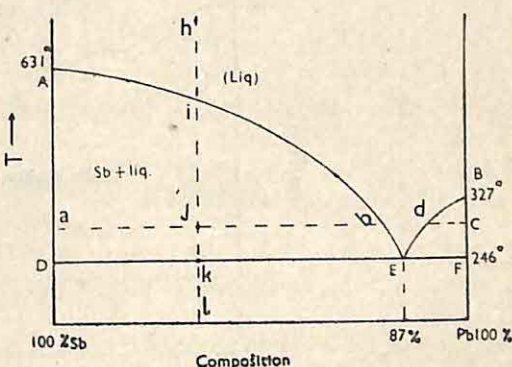


FIG. X.28 The phase diagram of Sb-Pb system

If we take the system as at point h (i.e., temp. about 700°C . and composition about 35% lead), the system will form a liquid phase only. If it is cooled, when the temperature comes down to the point i (about 550°C), crystals of antimony will begin to separate. On further cooling, say up to the point j (temp. about 300°C), appreciable quantities of Sb-crystals would separate which will remain in equilibrium with solution having a composition as at b (i.e., about 80% lead). The proportion of solid : solution = $bj : aj = 16 : 7$ (approx.). Further lowering of temperature below the point k , i.e., below 246°C , the remaining solution will solidify as the eutectic mixture of Sb and Pb-crystals. This gives us a picture of the behaviour of the system with change in temperature.

We may also examine the diagram as to the effect of adding a component in increasing amounts at constant temperature. Suppose we start with the system as at the point a , (temp. 300°C). It is pure antimony solid. If at constant temperature gradually increasing amounts of lead be added, the latter will melt and dissolve in it as much antimony as possible. The system will be composed of small amount of solution in equilibrium with solid antimony. The solution will have a composition as at b . When with addition of Pb the point j is reached, the amounts of solution : solid = $aj : bj$. If sufficient lead is added as to attain the composition at b , practically the whole of solid antimony would dissolve. On further increasing the proportion of lead, the system will be entirely liquid changing towards d as a single bivariant phase. At d , the solution is saturated with respect to lead and addition of lead will not produce any change. If at 300°C , pure lead is taken and gradually antimony is added, the system will change along cd , having Pb-crystals in eqm. with solution of composition as at d . The antimony will melt, though the temperature is quite low and dissolve lead to form a solution.

It will be seen in the next chapter that if N_1 be the conc. (mol-fraction) of a solute in an ideal solution then,

$$\log N_1 = \frac{-\Delta H_{\text{fusion}}}{2.303 R} \left[\frac{1}{T} - \frac{1}{T_0} \right]$$

where T and T_0 are the freezing points of the solution and of pure component. Calculated with this equation, the value of eutectic temperature is very near to the observed value of 246°C , which indicates that Pb-Sb solution behaves almost ideally.

Such simple eutectic systems are found not only in metal-metal systems, but also in salt systems, organic compounds or in salts and water systems. Two other typical examples are mentioned here.

The System Naphthalene-Salol.* The phase diagram of this system is given in Fig. X.29. The liquidus (AB and CB) and also the solidus are obtained from time-temperature cooling curves of different mixtures of the two components naphthalene (m.p. 80°) and salol (m.p. 42°). The system has exactly the same characteristics as observed in the case of Sb-Pb system. If a liquid mixture as at point x be cooled slowly, crystals of naphthalene begin to separate on reaching the point y .

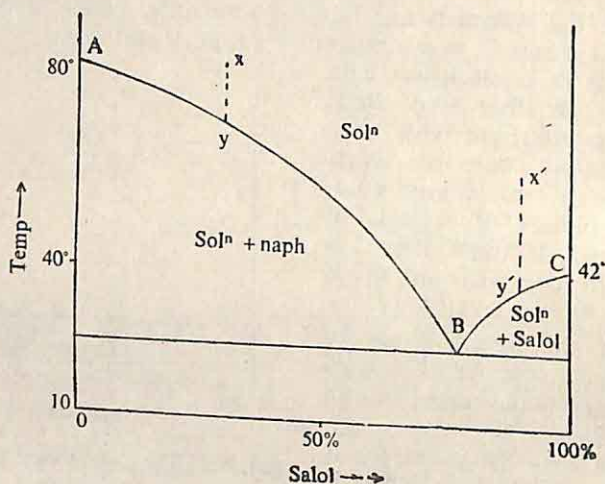


FIG. X.29 Phase-diagram of Naph.-salol system

These crystals are in eqm. with the solution. On further separation of crystals, as at point x' when cooled will produce crystals of salol at the point y' . The point B , where the freezing pt. curves AB and CB intersect, solid naphthalene, solid salol and the solution co-exist. It is thus the invariant eutectic point [composition 22% naph; temperature 25.4°C]. Below this temperature, no solution phase can exist.

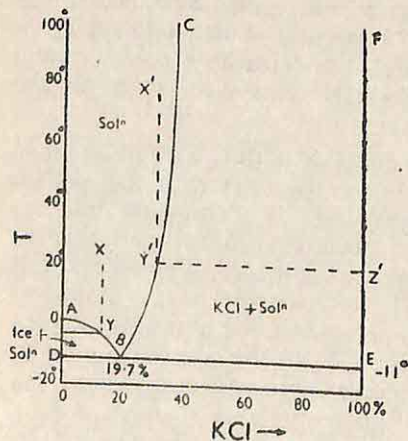


FIG. X.30 Phase diagram of KCl-H₂O system

The system H₂O-KCl. A careful study has revealed that water and potassium chloride system is a simple eutectic one. The phase diagram of this system is shown in Fig. X.30. The two components are not completely miscible in the solution phase in all proportions. That is why the curve liquidus BC cannot reach the other ordinate. There are two solid phases possible, KCl and ice (which can separate only below

* J. Ind. chem. Soc. 1955, 32, 157.

0°C). The liquidus in the diagram are denoted by AB , BC and the solidus by AD , DE and EF . On cooling a dilute solution of composition x , a temperature at the point y will be reached when ice crystals would separate out. The residual solution becomes richer in KCl and the freezing pt. changes along yB . At any point y in AB pure ice crystals will be in eqm. with a solution of KCl . At a temperature corresponding to D (-11°C), KCl -crystals also will begin to separate along with ice. On the other hand on cooling a concentrated solution of composition x' , KCl solid begins to separate at y' . As more and more KCl separates out, the composition of the saturated solution changes with temperature along $y'B$. Hence the liquidus CB is called the solubility curve of KCl in water.

At B , where the freezing point curve AB and the solubility curve CB meet, crystals of ice, KCl and also the solution exist together. Hence, the system is non-variant, for $F = C - P + 1 = 2 - 3 + 1 = 0$. This point B is therefore the eutectic point. ($T = -11^\circ\text{C}$, 19.7% KCl). In the case of systems where water is one of the components, the eutectic point is generally called the *cryohydric point*. The temperature at B is the cryohydric temperature and the solution of composition B is the cryohydric solution. The solid separating, on freezing, from a cryohydric solution is a mixture of the two solids and not a hydrate compound.

Below are enumerated some of the well studied simple eutectic systems.

TABLE : SIMPLE EUTECTIC SYSTEMS

A (°C)	Components		Eutectic temperature (°C)	A (°C)	Components		Eutectic temperature (°C)
		B. (°C)				B (°C)	
Bismuth	(317°)	Cadmium (321°)	146°	Benzene (5.4°)	methyl chloride	(-63.5°)	-79°
Zinc	(419°)	Cadmium (321°)	270°				
Gold	(1064°)	Thallium (303°)	131°	KI	water		-23°
KCl	(790°)	AgCl (451°)	306°	NH ₄ Cl	water		-15.4°
Na ₂ SO ₄	(881°)	NaCl (797°)	623°	NaNO ₃	water		-17.5°
O-nitrophenol (44°)	p-toluidine (43.6°)	15.6°		MgSO ₄	water		-3.9°

Binary systems with formation of compounds having congruent m.pt.

Type II. The two components of the systems which have been considered so far were such that they would not form any compound in the solid state ; on crystallisation pure components only would separate. But there are systems in which under suitable conditions of temperature and composition, compound formed from the components separates as a new solid phase. In such cases, the phase diagram has the appearance of two simple eutectic diagrams joined together, when the compound is stable enough up to its melting point. Such a substance which is stable up to the melting point and liquefies with the same composition is said to have a congruent melting point. The system of Sn and Mg is a typical example of this category.

X.26. The system Sn-Mg. The equilibrium diagram of tin (m.p. 232°) and magnesium (m.p. 651°) is shown in Fig. X.31. In this diagram P and W represent the freezing points of tin and magnesium. When magnesium is added to tin, the freezing point is lowered along PQ . The points on PQ represent the eqm. between crystals of tin and the liquid alloy. At Q (210°C), in addition to tin crystals, a new solid phase that of a compound of tin and magnesium begins to separate. This point Q is thus an invariant eutectic point having three phases (one liquid and two solids in equilibrium). Further addition of magnesium raises the freezing point along QR and the maximum is reached at R . All along QR from a molten alloy only solid compound will crystallise in eqm. with the liquid. At R , the composition of the liquid and of the solid phase (compound) is the same. This temperature (783°) is thus the congruent melting point of the compound. Thus PQ is the freezing pt. curve of tin and RQ is the freezing point curve of the compound. The molar composition corresponding to the point R reveals that the compound is Mg_2Sn . Apparently the two branches correspond to a simple eutectic diagram.

On further increasing the percentage of magnesium, the freezing point is lowered again along RS until we reach the second eutectic point S (565°C) where

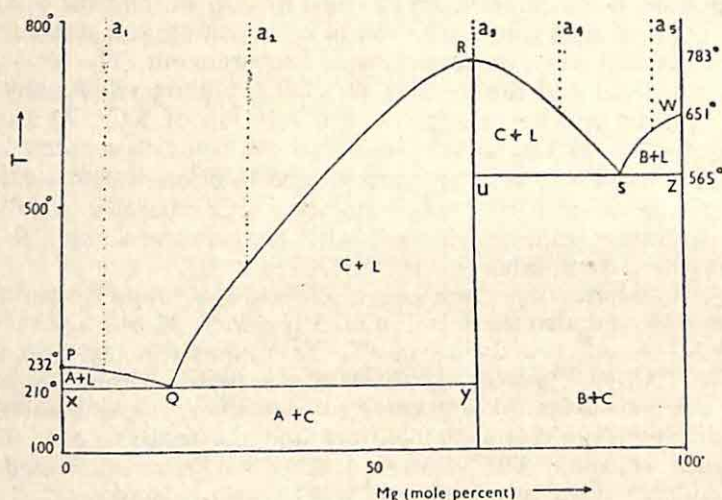


FIG. X.31 Phase diagram of the system Sn-Mg; A—Sn crystals; B—Mg crystals; C—compound Mg_2Sn ; L—liquid

two solids—the crystals of magnesium and those of the compound—are in equilibrium with the liquid phase. On further addition of Mg the freezing point will be raised along SW ; in other words if tin is added to pure magnesium, its m.pt. will be lowered along WS and on cooling only crystals of magnesium would separate till the point S is reached. The two branches RS and WS thus appear as a simple eutectic system.

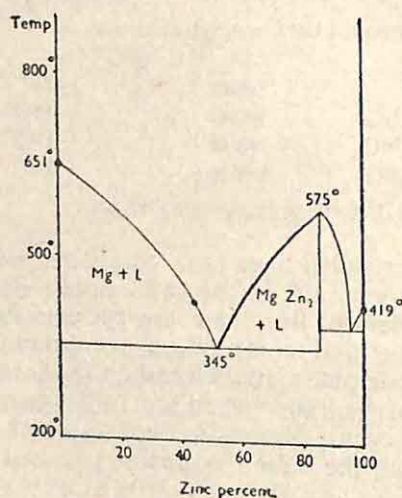


FIG. X.32 The system Mg-Zn

with an eutectic on either side. The existence of such a hump is indicative of the formation of a compound between the components in the solid phase. When the hump has a well-defined maximum, the compound formed is stable and has its melting point at the maximum.

The m. pts. and the eutectic pts. P , R , W and Q , S are invariant, whereas the system is monovariant in the areas PQX , RQY , RUS , WSZ , having a solid and a liquid phase co-existing. Below the solidus, we shall always have a conglomerate of crystals of the compound with magnesium or tin.

On cooling the homogeneous melt of different compositions say a_1 , a_2 , a_3 , a_4 and a_5 , the following phases would appear in the solid state :

Composition

a_1
 a_2 and a_4
 a_3
 a_5

Solid phase crystallising

Sn
 Compound Mg_2Sn
 Compound only
 Mg

The system Mg-Zn behaves exactly the same way, (Fig. X.32) producing a solid compound ($MgZn_2$, m.p. 575°). Many other systems including those of

organic compounds belong to this type, *e.g.*, urea-phenol, phenol-aniline, diphenylamine-benzophenone, acetone-phenol, ethyl iodide-ethyl ether, ethyl alcohol-acetaldehyde, NaF-MgF₂, Au-Sn, Al-Sn, etc. In fact, the formation of a compound in the solid state is being confirmed from the nature of the phase-equilibrium diagrams. Not only this, the range of the existence and the composition of the compound are also revealed from the diagram.

When more than one compound is formed, the number of humps in the liquidus will also be greater. There will occur as many humps as there are compounds formed. This is most convincingly illustrated by the two component system ferric chloride and water, in which several solid hydrates are known.

The system Fe₂Cl₆-H₂O. Four different crystalline hydrates of ferric chloride are known. All of these are quite stable, have congruent melting points and have their specific solubilities.

When small quantities of ferric chloride are added, the freezing pt. of water is lowered. The diagram of the system is shown in Fig. X.33. *AB* represents the freezing pt. curve along which crystals of ice separate. On increasing percentage of Fe₂Cl₆, ultimately the point *B* is reached at -55°C, when Fe₂Cl₆, 12H₂O crystals begin to separate. The point *B* is thus a eutectic point of solution, ice and Fe₂Cl₆, 12H₂O. Since one phase is solid ice, it is usually mentioned as a cryohydric point.

If solutions of ferric chloride be taken with compositions somewhat higher than that at *B*, the process of crystallisation would occur even at higher temperatures, so the curve *BCD* really represents the solubility curve of Fe₂Cl₆, 12H₂O, with a maximum at *C* (37°). At this point the liquid and the solid have identical composition and is thus the congruent melting point of dodecahydrate, Fe₂Cl₆, 12H₂O. From *C* to *D*, the solubility diminishes as the proportion of ferric chloride

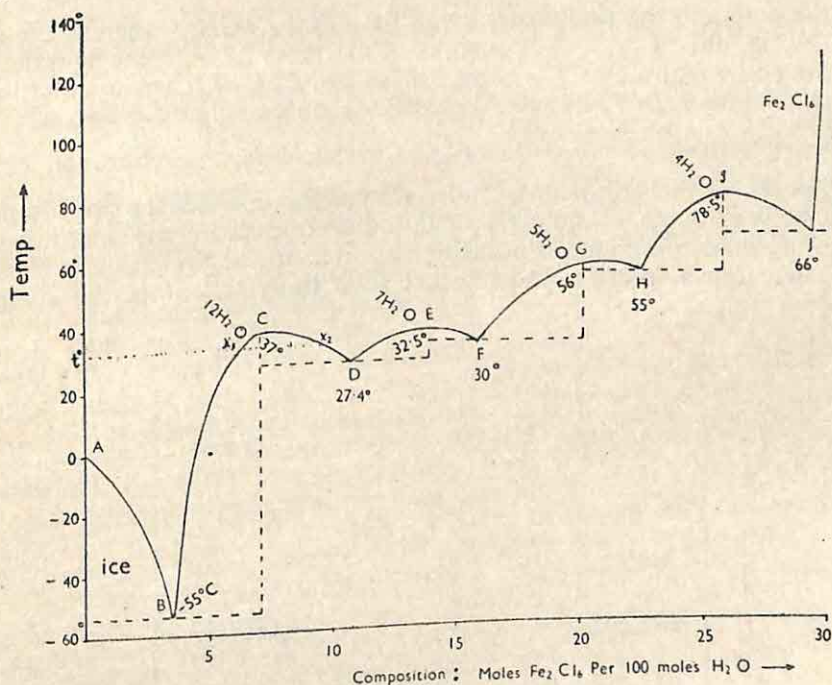


FIG. X.33 Phase diagrams of ferric chloride hydrates

Eutectic pts.

- B* = ice/Fe₂Cl₆, 12H₂O (-55°)
D = Fe₂Cl₆, 12H₂O/Fe₂Cl₆, 7H₂O (27.4°)
F = Fe₂Cl₆, 7H₂O/Fe₂Cl₆, 5H₂O (30°)
H = Fe₂Cl₆, 5H₂O/Fe₂Cl₆, 4H₂O (55°)
J = Fe₂Cl₆, 4H₂O/Fe₂Cl₆ (66°)

Congruent m. pts. (°C)

- C* Fe₂Cl₆, 12H₂O (37°)
E Fe₂Cl₆, 7H₂O (32.5°)
G Fe₂Cl₆, 5H₂O (56°)
I Fe₂Cl₆, 4H₂O (78.5°)

risers. There is thus a distinct hump with maximum at C , indicating the stable compound $\text{Fe}_2\text{Cl}_6, 12\text{H}_2\text{O}$ formation. When the amount of ferric chloride is raised enough to reach the composition as at D , another solid the heptahydrate, $\text{Fe}_2\text{Cl}_6, 7\text{H}_2\text{O}$, begins to crystallise. Pressure kept constant, this point D is a eutectic one having the liquid in equilibrium with two solid hydrates, $\text{Fe}_2\text{Cl}_6, 12\text{H}_2\text{O}$ and $\text{Fe}_2\text{Cl}_6, 7\text{H}_2\text{O}$.

Both the increase as also the decrease in the proportion of ferric chloride in the solution at C will cause a lowering of solubility, the solid phase crystallising out is $\text{Fe}_2\text{Cl}_6, 12\text{H}_2\text{O}$ on either side of C . The result is that at a temperature such as t° , the dodecahydrate has two distinct solubilities in water, x_1 and x_2 . Such a phenomenon is called *retroflex solubility* and is observed in systems producing solid compounds with congruent m. pts.

From solutions of ferric-chloride with concentrations higher than that at D , the heptahydrate crystals separate and the solubility curve DEF is like that of dodecahydrate. The point E is the maximum of this portion of the diagram and is the congruent melting point of the heptahydrate (32.5°). The point F (30°) is the eutectic point of hepta- and penta-hydrate crystals along with solution in equilibrium. On the right of F , the solutions will give, on cooling, crystals of pentahydrate. The solubility curve of the pentahydrate is FGH with the maximum at G (56°), the melting point of the pentahydrate crystals. There is yet another hydrate, the tetrahydrate $\text{Fe}_2\text{Cl}_6, 4\text{H}_2\text{O}$, which separates out from the liquid phase at H (55°). The point H is the eutectic point of penta-, tetrahydrate and solution. The solubility curve of tetrahydrate compound is similar to the previous one and is represented by HIJ . This compound melts at 78.5° , which is the maximum of this hump. At J we have the eutectic point of tetrahydrate, anhydrous Fe_2Cl_6 and solution. Beyond J , we have the steep solubility curve of anhydrous Fe_2Cl_6 .

In the diagram, the liquidus is given by $ABCDEFGHIJ$ whereas the solidus is given by the dotted lines. The regions of existence of different hydrated compounds are easily realisable. The congruent m.pts. C, E, G, I are invariant, so also the eutectic points B, D, F, H , and J ; the details are given in the diagram.

Binary systems with formation of compounds having incongruent m. pt.

X.27. Type III. In this group are included the systems in which the two components are completely miscible in liquid phase and also produce a compound in the solid state, but the solid compound is not stable up to its melting point. The compound breaks down into a solution and another solid (may be one of the component

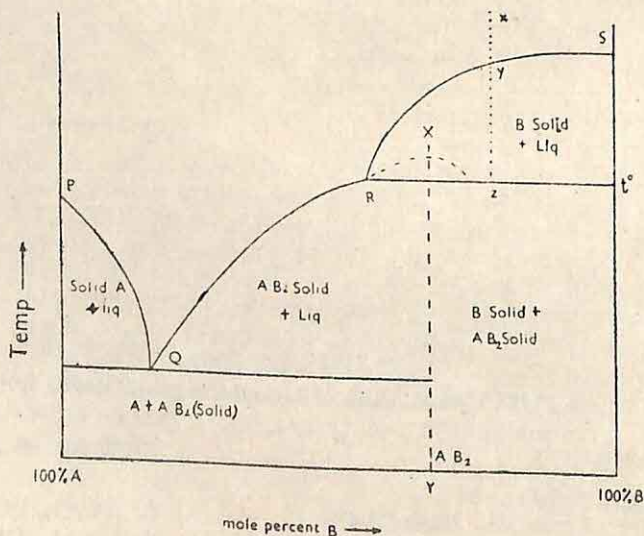
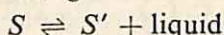


FIG. X.33(a) Eqm. diagram of a two component system forming a compound with incongruent m.pt.

solid) before reaching its own normal melting point. In other words when the compounds (S) is observed to melt, it produces a liquid phase of different composition and a new solid phase (S'). It is said to have an incongruent m. pt. and the change is called a *peritectic change*.



It is indeed melting with a chemical transformation.* We may first consider the general behaviour of such a system of two components A and B , which forms a solid compound say AB_2 with incongruent m.pt. Its phase diagram will have the general features as shown in Fig. X.33(a). In this diagram P and S are the melting points of the pure components and PQ and SR indicate the freezing pt. lowering when one component is added to the other. At the point Q , the amount of B added to A is just sufficient to produce crystals of a compound AB_2 along with solid A . That is, the point Q is the eutectic point of liquid, solid A and solid AB_2 . At temperatures below that of Q , only the solid phases, conglomerates of solid A and solid AB_2 , exist. Along QR , only the solid AB_2 separates from the solution. Had the compound been sufficiently stable with a congruent m. pt., the curve would have proceeded up to X , the maximum. In that event, X would have been the normal m.pt. of the compound. But before reaching that temperature, the compound AB_2 suffers a peritectic transformation at the point R producing the solid B and the solution. The point R is thus the point of intersection of the freezing point curves of the compound and that of the component B . When a liquid of composition x is gradually cooled, solid B begins to separate at y and thereafter as more and more B separates as solid the composition of the liquid changes along yR . When temp. t° is reached as at z , the liquid with composition R deposits AB_2 compound. On lowering the temperature slightly all B -solid slowly dissolves and are transformed into the compound AB_2 . This transformation occurs at a constant temperature. In the diagram are labelled the areas where different solids have their stability. We shall illustrate this with two hydrate systems.

The system $\text{NaCl-H}_2\text{O}$. The equilibrium diagram of this system is shown in Fig. X.34. With addition of NaCl the melting point of ice is lowered and the curve AB represents the freezing point lowering with increase in added NaCl . At B when the temperature is as low as -21°C , a new solid phase namely $\text{NaCl} \cdot 2\text{H}_2\text{O}$ also separates out from the solution along with ice. The point B is thus a eutectic point of solution/ice/ $\text{NaCl} \cdot 2\text{H}_2\text{O}$, often called the cryohydric point. Below this temperature, the system is only solid mixture of ice and $\text{NaCl} \cdot 2\text{H}_2\text{O}$. On further increase in the proportion of sodium chloride, the freezing point rises along BC until it reaches C (0.15°C). All along BC , the system is univariant having two phases $\text{NaCl} \cdot 2\text{H}_2\text{O}$ and solution in equilibrium. BC is the solubility curve of the dihydrate. It is clear if a solution of composition 'a' is cooled, we shall get ice crystals, whereas a solution of composition 'a'' on cooling will produce $\text{NaCl} \cdot 2\text{H}_2\text{O}$ crystals. At C , a peritectic change takes place. $\text{NaCl} \cdot 2\text{H}_2\text{O}$ solid is no longer stable above 0.15°C and it changes into anhydrous NaCl and the solution. The curve CD is the solubility curve of NaCl . The point C is the incongruent melting point of $\text{NaCl} \cdot 2\text{H}_2\text{O}$. The regions of stability of the different solid phases are indicated in the diagram.

Freezing mixtures. There are other facts which become obvious from the diagram. Firstly, we cannot have a solution of NaCl at a temperature lower than

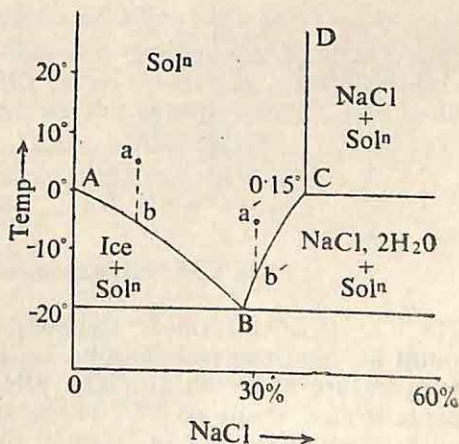


Fig. X.34 The system NaCl and H_2O

*Some authors name it a *meritectic change*.

the cryohydric temperature. Any solution taken to a lower temperature, being unstable, would change into a solid mixture of ice and $\text{NaCl} \cdot 2\text{H}_2\text{O}$. At a temperature above the cryohydric temperature, ice can exist in eqm. with solution of one composition and salt with solution of another composition.

Secondly, if we mix ice, salt and water at about say, 0°C water will dissolve the salt and if the saturated solution is quite concentrated, ice will begin to melt. In the melting of ice heat will be absorbed and temperature will go down. The salt solution, now being diluted, will dissolve more salt which will induce more ice to melt. In this way, due to abstraction of heat, temperature will fall till the cryohydric temperature -21°C is reached. The mixture will remain at this temperature until all the ice melts or all the salt dissolves. Ice and salt mixtures thus lead spontaneously to low temperatures, which is of wide application in domestic and commercial requirement as easily available freezing mixtures. Not only mixtures of common salt and ice serve as freezing mixtures but other salts with ice may also be used to attain low temperatures, *e.g.*, $\text{NH}_4\text{Cl}/\text{Ice}$ (-15°), $\text{NH}_4\text{NO}_3/\text{ice}$ (-17°), NaNO_3/ice (-18°), CaCl_2/ice (-55°), alcohol/solid CO_2 (-72°) etc.

The System $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$. The behaviour met with this system is graphically illustrated in Fig X.35. The possible solid phases are ice, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$; Na_2SO_4 , of which the heptahydrate is unstable in presence of the solution. On adding sodium sulphate to water, the freezing point is lowered. The curve AB is the freezing point curve, along which ice separates out from dilute solutions. When the concentration is increased to reach the point B , a new solid phase

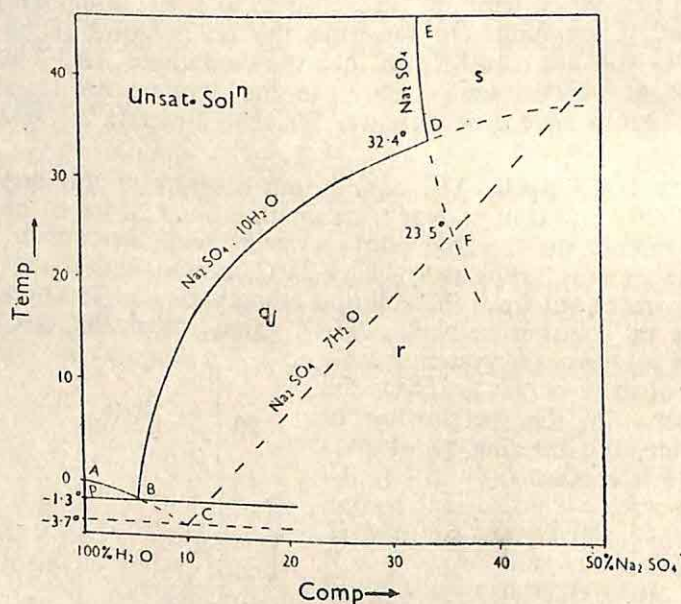
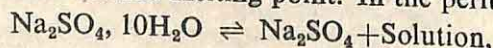


FIG. X.35 Phase diagram of sodium sulphate and water system

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is formed. The point B is then a non-variant eutectic or cryohydric point having three phases, solution, ice and decahydrate. The curve BD gives the temperature at which $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ separates out from comparatively more concentrated solutions. BD is the solubility curve for the decahydrate. At the point D , the decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ suffers a peritectic change, so the decahydrate does not reach its normal melting point. In the peritectic transformation,



the anhydrous solid Na_2SO_4 is obtained along with a solution of the salt. That is, D is the incongruent m.pt. of the compound $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and at this point there are three phases at equilibrium the solution, decahydrate and anhydrous solid Na_2SO_4 . Hence the point D represents a non-variant condition for the system; the temperature is 32.38°C , composition 33.2% Na_2SO_4 . Above this temperature,

the solid separating from saturated solutions is always anhydrous Na_2SO_4 . The curve DE is the solubility curve of anhydrous Na_2SO_4 .

When a saturated solution of sodium sulphate is cooled, along ED anhydrous salt separates. On reaching the point D , decahydrate crystals would begin to separate. This is rather a slow process and if a little alcohol is added, the deposit of decahydrate may be prevented and the saturated solution remains metastable and continues deposit of Na_2SO_4 till the point F is reached when heptahydrate crystals separate out at 23.5°C . This is formed only in absence of decahydrate and the heptahydrate has a spontaneous tendency to be transformed into decahydrate. The metastable conditions are indicated by broken lines. The curve CF denotes the solubility of heptahydrate. At F , the solid heptahydrate changes into anhydrous Na_2SO_4 and solution. So this is again an incongruent melting point, that of heptahydrate. Although the curves BD and CF can be followed, by super-saturation, beyond D and F to some extent but the point of equilibrium of the hepta and decahydrate with solution cannot be experimentally realised. As evident from the diagram the solubility of the metastable heptahydrate is more than that of the stable decahydrate, which is a thermodynamical necessity.

In the diagram, B and C are the non-variant cryohydric points, D and F are the non-variant incongruent melting points; the regions p , q , r and s are areas of equilibria of solution with ice, decahydrate, heptahydrate and anhydrous salt respectively.

Under higher pressures, if the temperature is raised to 234°C there would occur another transition in the crystalline form of anhydrous Na_2SO_4 from rhombic to monoclinic structure. This has not however been shown in the diagram.

Such peritectic transformations are noticed in many other binary systems such as, Au-Sn , Au-Sb , Mg-Ni , KCl-CuCl_2 , $\text{CaCl}_2\text{-CaF}_2$, $\text{CaF}_2\text{-BeF}_2$, $\text{K}_2\text{SO}_4\text{-CdSO}_4$, $\text{MgSO}_4\text{-H}_2\text{O}$, $\text{CaCl}_2\text{-H}_2\text{O}$, $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$, $\text{C}_6\text{H}_6\text{-Picric acid}$, $\text{SiO}_2\text{-Al}_2\text{O}_3$.

X.28. Type IV. Binary Systems with Solid Solutions which are Completely Miscible. In these systems neither pure components nor any compound of the two would separate out from the liquid phase. The two components are completely miscible both in the liquid and in the solid phase. The phase diagrams of such systems fall into three different groups.

- Intermediate freezing pt. systems.
- The freezing point shows a minimum.
- The freezing point shows a maximum.

(a) *Intermediate freezing point systems of solid solutions.*

The system Au-Pt. In the system Gold-Platinum, the two components are completely miscible in liquid phase and also form completely miscible solid solutions at all compositions. The behaviour of the system can be followed from the diagram given in Fig. X.36. The freezing point of pure gold is 1062°C and that of pure platinum 1755°C . The addition of Pt to Au raises the m.pt. whereas the addition of Au to Pt lowers the m.pt. The freezing pts. of all mixtures lie between the f.pt. of Au and Pt. This is also true of the m.pt. of all solid solutions. The upper curve in the diagram represents the liquidus and the lower curve the solidus. Thus the components form a continuous series of solid solutions with no maximum or minimum point of convergence of the two curves. It is easily understood that a liquid solution of composition, say x , is in equilibrium with a solid solution of composition x' . This happens at every temperature between the limits 1062° and 1755°C . Above the liquidus the system is entirely liquid and below the solidus the system is entirely solid. In the region in between the

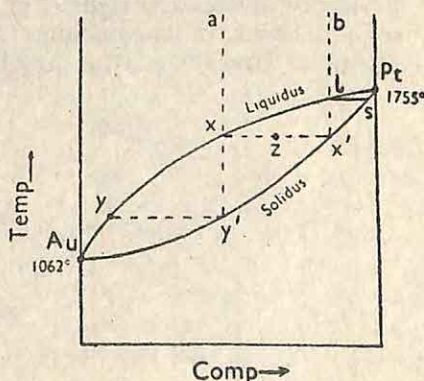


FIG. X.36 Phase-diagram of the system Pt-Au

solidus and liquidus the system would be partly liquid and partly solid. If the system be kept in a state represented by z , then it would be a mixture of liquid phase of composition x and solid phase x' in equilibrium.

If a Au-Pt melt of composition 'a' be slowly cooled, the first solid, which will indeed be a solid solution, will separate when the point x is reached. The composition of the solid separating out will be x' , i.e., richer in platinum. In consequence, the residual liquid phase will be richer in gold. The general principle is that *the concentration of the component by the addition of which freezing point is raised is greater in the solid than in the liquid phase*. On further cooling below x , more and more solid solution will separate out and the residual liquid in equilibrium will be deprived more and more of its platinum. The composition of the liquid solution will move along xy while that of the solid solution along $x'y'$. At y' vertically below x , the system entirely solidifies and just at the moment of complete solidification, the liquid composition is x' and solid composition y' .

Such behaviour also explains the fractional crystallisation of the components. The solid separating at x' , if removed, melted and again cooled, solid solution will separate out at l and will have the composition s , in which Pt-content will be much higher. The process could be repeated with the solid s , until the component Pt is reached. On the other hand, by taking the liquid fractions at y , a successive repetition would enable us to obtain liquid fractions with higher and higher percentage of gold and ultimately pure gold would separate out. Both the components are thus available in pure forms from such a system by fractional crystallisation.

In a system of this nature two phases can co-exist always and hence the system is monovariant. No invariant point is available in the system.

There are many systems with such continuous series of solid solutions; e.g., Cu-Ni, CO-Ni, Bi-Sb, Ag-Pd, Ag-Au, AgCl-NaCl, PbBr₂-PbCl₂, KCNS-NH₄CNS, naphthalene- β -naphthol etc.

(b) *Solid solutions with a minimum freezing point.* There are some binary systems in which the solid solutions obtained are completely miscible and these solid solutions exhibit freezing point curves with a minimum. In these cases, the freezing point is lowered when A is added to B or B to A . A typical case is provided by the system HgBr₂-HgI₂, shown graphically in Fig. X.37(b). The upper curve is the liquidus and the lower curve solidus. The m.pt. of HgBr₂ is 236°C and that of HgI₂ is 255°C. The liquidus and the solidus touch at the point X , where the compositions of the solid solution and the liquid solution are identical. So the solid solution will melt at this point sharply without any change in composition like a pure compound. At any other temperature, a liquid will be in equilibrium with a solid solution of different composition. A little inspection of the curves will show that a system having composition on the left of X can be fractionally crystallised into pure HgBr₂ and solid solution of composition X . Again a system with a composition on the right of X can be fractionally separated into HgI₂ and the solid solution of composition X . Both the components cannot be fractionally separated from the mixture simultaneously.

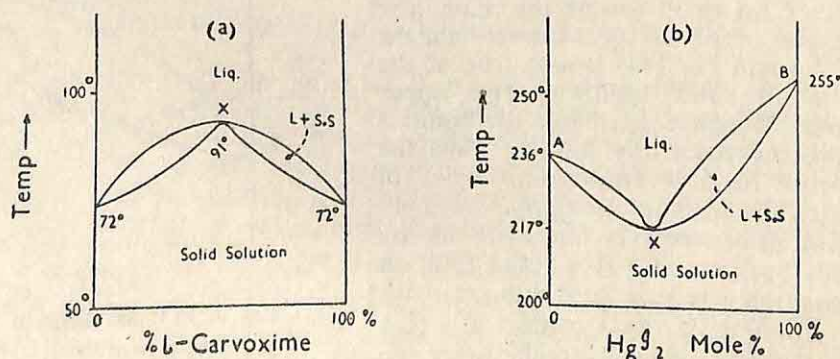


FIG. X.37 Phase diagram of completely miscible solid solutions (a) *d*- and *l*-carvoxime with maximum *f. pt.* (b) HgBr₂-HgI₂ with minimum *f. pt.*

The system Cu-Ag. Copper melts at 1084°C and silver at 960°C . The two components are completely miscible in liquid phase but they form solid solutions which are only partially miscible. The phase diagram of the system is given in

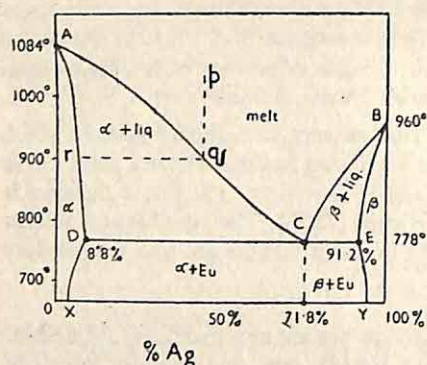


FIG. X.39 Phase diagram of Cu-Ag system

sequence the melt would be silver rich and with further cooling the composition of the liquid will proceed along qC until the point C is reached.

On the other hand, addition of copper to silver will lower the freezing point of the latter along BC ; the solid separating will be a solid solution of copper in silver, say β -phase. The composition of the β -phase is represented by BE . In the area BEC , β -phase is in equilibrium with the melt. On the right of BE , only solid β -phase can exist.

The liquidus AC and BC meet at C , where α -, β - and liquid phases can co-exist in equilibrium. Hence the point is an invariant one [$F = 2 - 3 + 1 = 0$], the pressure being kept constant. The point is thus the eutectic point of the Cu-Ag system having a composition of 71.8% Ag and a temperature of 778°C . Below this temperature, liquid phase cannot exist.

A mixture of 71.8% Ag will melt or solidify sharply at 778°C like a pure metal. But a melt of composition less than 71.8% Ag will give on cooling below 778°C a heterogeneous mixture of α -phase and eutectic. On the other hand, a mixture having Ag-content higher than 71.8% on cooling below 778°C will produce a heterogeneous mixture of β -phase with eutectic. The variation of composition of α - and β -phases with temperature below eutectic temperature are represented by DX and EY .

(ii). **Peritectic system of partially miscible solid solutions.** The system Hg-Cd. This system provides a suitable illustration of partially miscible solid solutions in which the solid solutions may undergo a peritectic transformation at a definite temperature. The behaviour of the system with change in temperature can be followed from the phase diagram shown in Fig. X.40. Hg melts at -39°C and Cd at 320°C . Addition of mercury to cadmium lowers the freezing point (shown by AQ) while addition of cadmium to mercury raises the freezing point (shown by BQ). In this diagram BQ and BS are the liquidus and solidus of the α -solid solution of Cd in Hg; whereas AQ and AR are the liquidus and solidus of the β -solid solution of Hg in Cd. It is easily seen that any melt having composition between B and Q will deposit only α -solid solution. A melt with a composition between A and R will deposit only β -solid solution. At 182°C , α -solid has the composition as at S , the β -solid as at R , and at this temperature the melt has the composition as at Q . Hence at this temperature, three phases may remain in equilibrium, i.e., $F = 2 - 3 + 1 = 0$. This makes the horizontal line QSR .

On cooling a melt of composition ' a ', β -phase of composition ' b ' will separate out when the point ' b ' is reached. Further lowering of temperature will produce more β -phase. The composition of β -phase changes along $b'R$ and that of the residual melt along $b'Q$. On reaching a temperature corresponding to c (182°C), α -phase also begins to appear. If more heat is abstracted, β -phase will undergo a peritectic transformation with the liquid to produce the α -phase, the temperature remaining unaltered. This will continue until the liquid phase disappears. The

composition of the α -phase is given by S and that of β -phase by R . As the two conjugate solutions are cooled below 182°C , we pass into the area of partial miscibility ; two solid solutions remaining in a mixture. The lines SX and RY give the change in composition of the α - and β -solid solutions with temperature.

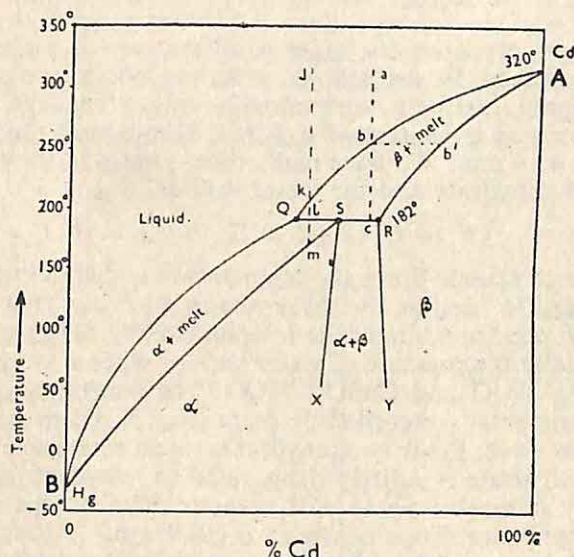


FIG. X.40 Equilibrium diagram of the system Hg-Cd (Peritectic).

On cooling a melt from the point j (lying between Q and S), β -phase will begin to separate at k . On reaching the point l , the peritectic reaction sets in. β -phase will be changed into α -phase. But as the proportion of mercury is more than that required for the composition at S , some liquid will be still left. On lowering the temperature further α -crystals would separate out until the point m is reached, when the system would entirely solidify as α -phase.

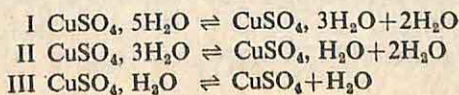
Such peritectics of two solid solutions are found in binary systems such as Co-Fe, AgNO_3 - NaNO_3 , LiCl - AgCl , $p\text{-C}_6\text{H}_4\text{ICl}$ - $p\text{-C}_6\text{H}_4\text{I}_2$.

There are also systems in which the components are not completely miscible in the liquid state and yield either pure components or solid solutions on crystallisation. For such systems, the student may consult some treatise on "phase rule" such as that of "Findlay, Campbell and Smith".

SOLID-GAS PHASES

X.30. Binary systems, in which solid and gas phases are present, become of notable importance when the two components form one or more compounds in the solid phase. Such cases are found in salt hydrates and compounds like argentamino chlorides (AgCl , $x\text{NH}_3$) etc. In studying the equilibria in such systems it is convenient to follow up the pressure variations with composition. We may exemplify this with the salt-hydrate system CuSO_4 and H_2O .

With these two components— CuSO_4 and H_2O —there are, under different conditions, four solid phases and the vapour phase is one of water. The solid phases are (i) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (ii) $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, (iii) $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and (iv) anhydrous CuSO_4 . When water vapour is gradually led into the system containing anhydrous CuSO_4 or when the pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is gradually dehydrated, the following equilibria are envisaged :



eqm constants

$$\begin{aligned} K_1 &= P_I = 45.4 \text{ mm} \\ K_2 &= P_{II} = 30.9 \text{ mm} \\ K_3 &= P_{III} = 4.5 \text{ mm} \end{aligned}$$

If P_I , P_{II} and P_{III} denote the corresponding equilibrium pressures of water vapour, applying law of mass action, we know that

$$\frac{P_I^2 \times P_{tr}}{P_{penta}} = K_1' \text{ or } P_I = K_1$$

Similarly, the vapour pressures for other equilibria are also constant at a given temperature. This indeed is realised in practice. When pentahydrate crystals are enclosed in a vessel, kept at a constant temperature (say 50°C) and the vapour is continuously removed by means of a pump, the vapour pressure is found to remain constant at 45.4 mm. We have really three phases in the system now, solid pentahydrate, solid trihydrate and the water vapour. So,

$$F = C - P + 2 = 2 - 3 + 2 = 1$$

i.e., the system is univariant. Since the temperature is defined to be constant, the pressure cannot vary so long as the three phases co-exist. This pressure is often mentioned as the vapour pressure of the hydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ which is somewhat misleading. It is really the pressure of water vapour when it is in equilibrium with two phases $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$. The constancy of the pressure is shown in the experimentally recorded diagram (Fig. X.41) in which along ab the equilibrium pressures over the tri-pentahydrate system remains constant.

At b the pentahydrate is entirely dehydrated to trihydrate and as the system now contains only one solid phase with vapour. The system is now bivariant. At this stage the pressure drops down to c (30.9 mm). Along cd , the pressure again remains constant as trihydrate loses water and is slowly dehydrated to monohydrate ($F = 1$). When the point d is reached, the composition shows it as only monohydrate, the system becomes bivariant and the pressure falls to e (4.4 mm).

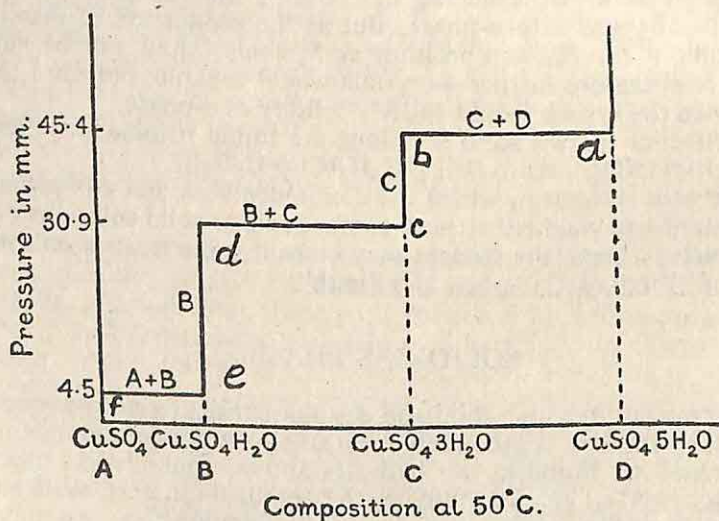


FIG. X.41 The dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 50°C

With continued removal of H_2O -vapour, the monohydrate crystals are slowly converted into anhydrous sulphate along ef . The pressure during the process remains constant, for, again two solids and one vapour phase remain together to make the system univariant. When the whole of water is removed, the pressure drops down to zero.

The diagram has a stepwise configuration. Such step-wise vapour-pressure-composition diagrams are indicative of the formation of compounds between the components which may not be isolated or prepared experimentally. The number of steps would also indicate the number of compounds formed between the components.

The pressure-composition curve of the system containing AgCl and ammonia is given in Fig. X.41(a). The three steps are indicative of three compounds between them, viz. $\text{AgCl} \cdot 3\text{NH}_3$; $2\text{AgCl} \cdot 3\text{NH}_3$; $\text{AgCl} \cdot \text{NH}_3$.

The behaviour of such systems can also be expressed by means of pressure-temperature diagrams. For the copper sulphate system, the curves are given in Fig. X.42. The topmost curve is the vapour-pressure curve of pentahydrate. Since, as already stated there are two solids and a vapour, the system is univariant. As such, the variation of pressure with temperature will follow the same pattern as the vapour pressure of pure liquid. The other two equilibria for tri- and monohydrates are also univariant and their behaviours are also similar.

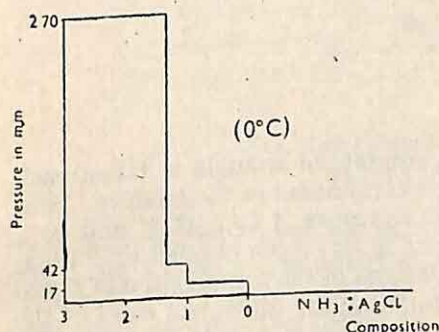


FIG. X.41(a) Dissociation pressures of argentammino chloride

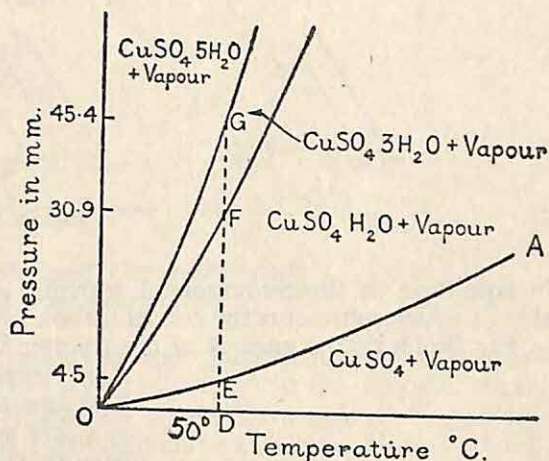


FIG. X.42 Vapour pressure curves of copper sulphate hydrate

Deliquescence and Efflorescence. When a crystalline substance on standing in air forms a solution by absorbing water vapour from the atmosphere it is said to deliquesce. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{NaOH} \cdot \text{H}_2\text{O}$ etc. are highly deliquescent.

In our laboratories the temperature is about 20°C so that the vapour pressure of water is about 14 mm. If some $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ be kept exposed in air, it absorbs water and as it is highly soluble, a saturated solution is formed. The vapour pressure of sat. solution of calcium chloride is quite low, about 7-8 mm, at 20°C . This is much lower than the vapour pressure of water in the atmosphere. The result is, more and more water is absorbed and the solution becomes more and more dilute. This continues till the vap-pressure of the solution is equal to that of the water in the atmosphere. Hence a substance to behave as deliquescent must be a very soluble one having a low vapour pressure of its saturated solution.

On the other hand there are hydrated crystals such as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, sodium carbonate decahydrate, which give up their water of hydration to the atmosphere and in the process disintegrate into dehydrated products, spontaneously. This is due to the fact that these hydrated crystals have vapour pressures greater than that of water in the atmosphere at room temperature. Thus $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ crystals have eqm. vapour pressure of about 24 mm whereas the vapour pressure of water at 20° is about 14 mm. Hence water escapes as vapour spontaneously from the decahydrate transforming it into monohydrate. This phenomenon is efflorescence.

THREE COMPONENT SYSTEMS

X.31. In a ternary system if all the three components form a homogeneous single phase, which is the minimum number of phases, the degrees of freedom will be maximum i.e., 4,

$$F = 3 + 2 - P = 5 - 1 = 4.$$

phase. This is an invariant ternary eutectic point, under a constant pressure, (vapour being neglected).

$$F = C - P + 1 = 3 - 4 + 1 = 0$$

The cooling curve of such ternary mixtures will be characterised by three arrests, the first for freezing of first component, the second arrest indicating the separations of the second component and the last arrest indicating the separation of all the three i.e., the ternary eutectic mixture.

When only one solid separates from the ternary liquid, there are two phases in equilibrium and hence the system is bivariant. This should be represented by

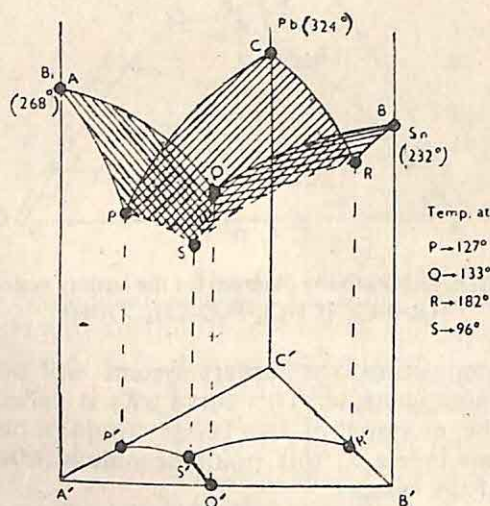


FIG. X.46 Space model of a ternary eutectic system

a surface. In this diagram, the surfaces $AQSP$, $BQSR$, $CPSR$ represent the conditions for separation of Bi, Sn and Pb respectively from the liquid phase. The lines where two surfaces meet constitute the ternary eutectic curves. These lines PS , QS , RS indicate the conditions for the separation of two solid phases in eqm. with the liquid phase. When the ternary-eutectic curves are projected on the base of the space-model, the nature of the curves would be given by $P'S'$, $Q'S'$, $R'S'$.

Systems of this type are found in alloys and glasses. But complexities arise due to compound formation or solid solutions and polymorphic changes. Ternary systems like $\text{KNO}_3\text{-LiNO}_3\text{-NaNO}_3$, or diphenyl-naphthalene-salol have equilibria which can be represented satisfactorily by curves of the type Fig. X.46.

References for further reading

- (i) *The Phase Rule and its applications* : FINDLAY, CAMPBELL AND SMITH
- (ii) *The Phase Rule and phase relations* : BOWDEN
- (iii) *Treatise on physical chemistry, chap. IX* : TAYLOR AND TAYLOR
- (iv) *An introduction to phase rule* : DEMING, J. CHEM. EDN. 1939, 16, 215, 260
- (v) *Bockris et al* : TRANS. FARADAY. SOC. 1951, 47, 184.

Questions

1. The distribution coefficient of iodine between water and CS_2 is 1.7×10^{-3} . One litre of aqueous solution containing 1 gm of iodine is shaken with 50 c.c. of CS_2 . What will be the residual concentration of iodine in water? If 50 c.c. of CS_2 were used in five successive quantities of 10 c.c. each, what would be concentration of iodine remaining in water?

[Ans. (a) 3.29×10^{-3} (b) 6.5×10^{-5} gm/l]

2. A mixture of water and nitrobenzene boils at 99°C , what would be their respective weights in the distillate? (vap. pr. of water at $99^\circ\text{C} = 733$ mm.)

(Ans. 1:3.94)

3. Raoult's law is obeyed by a mixture of benzene and toluene. A mixture of the two containing 0.34 mol-fraction of toluene boils at 88°C . The vapour pressures of pure benzene and toluene at this temperature are 960 mm and 380 mm respectively. Find out the composition of the vapour formed on its boiling. [Ans. benzene, 0.83 mol-fraction]

4. A pure substance can exist in a gas phase, liquid phase and two solid modifications. How many one-, two or three-phase equilibria are possible? Can all the four phases remain in equilibrium?

5. State how many degrees of freedom will be possessed by each of the following systems,

- (i) an aqueous solution of ZnSO_4 (ii) PCl_5 -vapour
- (iii) solid camphor in eqm with its vapour
- (iv) sugar(s) in eqm with its saturated solution at 25°C .

6. Explain why

- (a) 'fusion mixture' is used instead of Na_2CO_3 in dry tests
- (b) a mixture of tin and lead is used for soldering
- (c) on heating iodine sublimes but sulphur melts at ord. pressure
- (d) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is efflorescent but $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is deliquescent
- (e) ice and salt mixture is used as refrigerant.

7. Define, with suitable illustrations,

- (a) critical solution temperature. (b) azeotropes (c) cryohydrate
- (d) peritectic change (e) enantiotropism.

8. Draw phase diagrams indicating the behaviour of a mixture of two miscible liquids on distillation,

(a) if only one of them can be separated in pure state and (b) if both of them can be separated.

9. Discuss the behaviour of a liquid melt of two metallic components on cooling (a) when no compound is formed (b) when compounds are formed.

10. What types of phase diagrams would you construct for a system of water and a salt which gives two or more hydrates? What informations can be obtained from these diagrams?

DILUTE SOLUTIONS : COLLIGATIVE PROPERTIES

A colligative property of a system is one which depends only on the number of particles present and not on the nature of the particles. Dilute solutions provide us with illustrations where many of their properties are colligative. The addition of a solute lowers the free energy of the solution and we shall see that other properties are thereby affected ; the vapour-pressure is lowered, the boiling point is raised, the freezing point is depressed and so on. The extent or magnitude of these changes brought about in the solution is dependent only on the number of solute particles. Hence these properties of the solutions are termed *colligative properties*.

It is easy to develop quantitative relations between these properties (e.g., freezing pt. depression) and the number of particles present in the solution *i.e.*, concentration of the solute. We shall always consider here solutions of *non-volatile* solutes so that the vapour-pressure of the solute is negligible. Moreover, at first, only the non-electrolyte solutes will be dealt with. Subsequently we shall study the effects that arise when the solutes taken are electrolytes suffering dissociation in the solvent used.

XI.1. Concentration Units. The relative amount of a substance present in a solution or a mixture is known as its *concentration*. The concentration can be expressed in different units or measures. In studying solubilities or in phase diagrams, we have often expressed the proportion of a component on percentage basis, *i.e.*, number of parts of the component in 100 parts of the mixture. Besides this, there are at least four other sets of units commonly used.

(a) *Molarity*. The molarity of a solution is the number of gm-moles of solute present in 1 litre of solution. It is the most widely used unit employed for expressing concentration. A 0.1M CaCl_2 solution contains 0.1 gm-mole of the salt per litre of the solution ; the conc. of Ca^{++} is also 0.1 M and that of Cl^- ion is 0.2 M (assuming complete dissociation).

(b) *Molality*. The molality of a solution is the number of gm-moles of solute present in 1000 gms of the solvent. The molality is often symbolised by letter "*m*". Thus, 0.1 *m* urea solution in alcohol will mean 0.1 gm-mole of urea dissolved in 1000 gms of alcohol. This unit is used in dealing with freezing point and boiling point calculations.

(c) *Normality*. The gm-equivalent of a substance is the weight that would produce, or react with, 7.999 gms of oxygen or 1.008 gms of hydrogen. The normality of a solution is the number of gm-equivalent weights of the solute present per litre of the solution. The equivalent weight of Mg^{++} is $24.3/2.016$ (or 12.05), since 24.3 gms of Mg displaces 2.016 gms of hydrogen from an acid. A 0.1N solution of Mg-ion will therefore contain 1.205 gms of Mg^{++} per litre of the solution. This unit is used mostly in volumetric analysis.

(d) *Mol-fraction*. In this system, the relative amount of a component in a mixture is expressed as a fraction of the total amount of all the components, the amounts of every component being measured in gm-molecules. To illustrate : suppose in a solution there are present n_1 gm-moles of A and n_2 gm-moles of B, *i.e.*, total amount is $n_1 + n_2$ gm-moles. Then,

$$\text{the mol-fraction of component A} = \frac{n_1}{n_1 + n_2} = x_1 \text{ (say)}$$

$$\text{and the mol-fraction of component B} = \frac{n_2}{n_1 + n_2} = x_2 \text{ (say)}$$

Generally speaking, if there are i -components present in the solution, then

$$x_1 = \frac{n_1}{n_1 + n_2 + \dots + n_i} = \frac{n_1}{\sum n_i}$$

$$x_2 = \frac{n_2}{n_1 + n_2 + \dots + n_i} = \frac{n_2}{\sum n_i}$$

$$x_i = \frac{n_i}{n_1 + n_2 + \dots + n_i} = \frac{n_i}{\sum n_i}$$

It is obvious that sum of the mol-fractions of all the components would be unity,

$$x_1 + x_2 + x_3 + \dots + x_i = 1$$

This unit is convenient when a property of a system requires to be expressed in terms of relative amounts of solute and solvent.

XI.2. Lowering of Vapour Pressure of Solutions. The colligative properties of dilute solutions primarily stem from the validity of Raoult's law for the solvent. When the solution is dilute the solute molecules are sufficiently separated and the solution is supposed to behave ideally.

Consider a solution obtained from a non-volatile solute dissolved in a liquid (solvent). We shall denote the parameters of the solvent with suffix 1 and those of the solute with suffix 2. It is common knowledge that

(i) The presence of solute will lower the vapour pressure of the solvent over the solution at any temperature, and

(ii) The vapour pressure of the solvent over the pure solvent or over the solution always increases with rise in temperature.

These are graphically presented in Fig. XI.1.

The quantitative relation between the vapour pressure of a component and its concentration in a solution is given by the Raoult's law in ideal systems. Assuming dilute solutions to behave ideally, we have

$$p_1 = x_1 p_1^0 \quad \dots \quad (XI.1)$$

where p_1 is the vapour pressure of the solvent over the solution and p_1^0 is the vapour pressure of pure solvent at a given temperature, x_1 is the mol-fraction of the solvent in the solution. As the solute is non-volatile, p_1 is indeed the vapour-pressure of the solution.

Now x_1 is less than unity, hence p_1 is always less than p_1^0 , i.e., the vapour pressure of the solution is less than that of the pure solvent. Rewriting eqn. XI.1,

$$p_1 = (1 - x_2) p_1^0$$

where x_2 is the mol-fraction of the non-volatile solute.

Suffix 1 is used for solvents and suffix 2 for the solute

Therefore

$$\frac{p_1^0 - p_1}{p_1^0} = x_2$$

or

$$\frac{\Delta p}{p_1^0} = x_2$$

$\dots \quad (XI.2)$

Raoult's law, in this form, may be stated as that *in dilute solutions the relative lowering of vapour-pressure of the solvent is equal to the mol-fraction of the solute.*

We have

$$\frac{p_1^0 - p_1}{p_1^0} = x_2 = \frac{n_2}{n_1 + n_2}$$

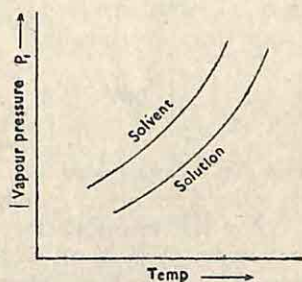


FIG. XI.1 Vap-pressure and temperature of pure solvent and solution

n_1, n_2 are the gm-moles of solvent and solute respectively. For a dilute solution, $n_1 \gg n_2$, hence

$$\frac{\Delta p}{p_1^0} \approx \frac{n_2}{n_1}$$

For a definite quantity of a given solvent, n_1 and p_1^0 are both constants,

$$\text{i.e., } \Delta p \propto n_2$$

which means that *equimolecular quantities of any non-volatile solute dissolved in the same quantity of the same solvent will produce the same lowering of vapour pressure*. This indeed is a direct consequence from the Raoult's law. The lowering of vapour-pressure is thus a colligative property as it depends only on the amount of the solute *i.e.*, the number of molecules and not on their nature.

XI.3. Measurement of Vapour-Pressure : Isoteniscope. Of the various methods used for determination of vapour pressure, the use of isoteniscope provides a convenient one which yields good and precise results. An arrangement is shown in Fig. XI.2. In a small bulb *A*, some liquid or solution is taken. The bulb is connected with a U-tube (*B*) and kept in a bath whose temperature is controlled. The upper part of the U-tube is surrounded with a condenser and the tube is also attached to a manometer and pump. The liquid is boiled until the air in space *C* above the liquid is displaced by its vapour. On cooling, some liquid condenses in *B* and there is vapour in the space *C*. The apparatus is kept in a thermostat until it attains the desired temperature. The pressure of the vapour in space *C* is the vapour pressure of the liquid in *A* at the temperature of the thermostat. The external pressure is then adjusted with the help of a pump until the liquid levels in the two limbs of the U-tube are the same. When this is attained, the reading of the manometer gives the pressure of the vapour in the bulb *A*. In this way taking pure solvent and the solution both p_1^0 and p_1 can be measured to obtain Δp .

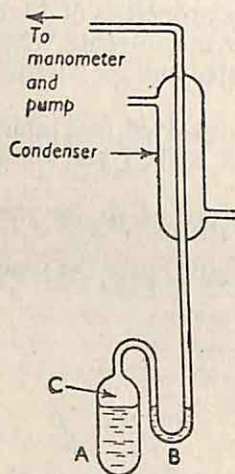


FIG. XI.2: Isoteniscope

XI.4. Measurement of Vap-pressure Lowering. By the Ostwald-Walker method, the relative lowering of vapour pressure can be obtained without measuring the vapour pressures of solution and of solvent separately. The method may be outlined as follows.

A stream of dry air is slowly passed through a previously weighed series of bulbs containing the solution (Fig. XI.3). The air takes up vapour from the solution until it is saturated up to pressure p_1 , which is the vapour-pressure of the solution at that temperature. The actual loss of vapour from the bulb is obtained by subsequently weighing the bulb. The loss of weight w_1 is proportional to p_1 , *i.e.*, $w_1 = kp_1$.

The air (already saturated with vapour up to pressure p_1) is next passed through another series of bulbs, also previously weighed and containing pure solvent. Since the vapour pressure

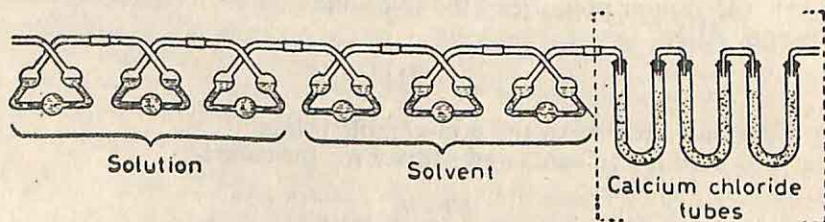


FIG. XI.3 Ostwald-Walker method for measuring vap-pressure lowering

of pure solvent p_1^0 is greater than p_1 , the air will take up some more vapour from pure solvent until the air is saturated to pressure p_1^0 . The bulbs are weighed again to obtain the loss of weight, w_2 , which is required to saturate the air from pressure p_1 to p_1^0 .

$$\therefore w_2 \text{ is proportional to } p_1^0 - p_1, \text{ i.e., } w_2 = k(p_1^0 - p_1)$$

Finally the air is passed through a weighed series of U-tubes containing an absorbent for the vapour of the solvent, *e.g.*, anhydrous CaCl_2 if the solvent is water. The increase in weight of the

U-tubes is determined, which gives $w_1 + w_2$. This weight is the measure of the vapour required to saturate the air up to pressure p_1^0 .

$$\text{Hence} \quad \frac{p_1^0 - p_1}{p_1^0} = \frac{w_2/k}{(w_1 + w_2)/k} = \frac{w_2}{w_1 + w_2}$$

Since the quantities on the right-hand side are known the relative lowering of vapour-pressure is obtained. The temperature must be kept constant throughout.

XI.5. Elevation of Boiling Point of Solutions. The vapour pressure of a pure solvent increases with rise in temperature. This is shown by AB in Fig. XI.4. When a non-volatile solute is dissolved in the solvent, the vap-pressure of the solution will be lower than that of the pure solvent at any given temperature. Here also the vapour pressure of the solution increases with rise in temperature as shown by CD in the figure.

A liquid boils when its vapour-pressure becomes equal to that of the super-incumbent pressure. Let T_b be the boiling temperature of the pure solvent and so its vapour pressure equals one atmosphere at this temperature. But at this temperature the solution will have a vapour pressure lower than one atmosphere and hence it will not boil. With further increase in temperature, say to T_b' , the vapour-pressure over the solution rises to one atmosphere when the solution would boil. This means that *the solution has a higher boiling point than that of the pure solvent*. The increase in boiling temperature is given by $PR = T_b' - T_b = \Delta T$, and increase in pressure is given by $PQ = p_1^0 - p_1 = \Delta p$. As the solutions are dilute, ΔT and Δp are small quantities.

In the solution vapour-pressure curve CD, at the point Q, the pressure is p_1 and temperature is T_b . At the point R, the pressure is p_1^0 and temperature is T_b' . We can apply Clausius-Clapeyron equation at these points and write,

$$\ln p_1 = -\frac{L_v}{RT_b} + Z (\text{constant}) ; \quad \ln p_1^0 = -\frac{L_v}{RT_b'} + Z (\text{constant})$$

$$\text{i.e.,} \quad \ln \frac{p_1}{p_1^0} = -\frac{L_v}{R} \left[\frac{1}{T_b} - \frac{1}{T_b'} \right] = -\frac{L_v}{R} \cdot \frac{T_b' - T_b}{T_b T_b'}$$

where L_v is the molar latent heat of vaporisation. We may also write,

$$\ln \left(1 - \frac{p_1^0 - p_1}{p_1^0} \right) = -\frac{L_v}{R} \cdot \frac{\Delta T}{T_b^2} \quad (T_b \text{ is very close to } T_b', \text{ hence } T_b T_b' \approx T_b^2)$$

$$\text{or,} \quad \ln \left(1 - \frac{\Delta p}{p_1^0} \right) = -\frac{L_v}{R} \cdot \frac{\Delta T}{T_b^2}$$

Since $\frac{\Delta p}{p_1^0}$ is quite small, expanding and neglecting higher powers,

$$-\frac{\Delta p}{p_1^0} = -\frac{L_v}{R} \cdot \frac{\Delta T}{T_b^2}$$

But from Raoult's law, we know, $\frac{\Delta p}{p_1^0} = x_2$ (mol-fraction of the solute).

$$\therefore \quad x_2 = \frac{L_v}{R} \cdot \frac{\Delta T}{T_b^2}$$

or

$$\Delta T = \frac{RT_b^2}{L_v} \cdot x_2 \quad \dots (X.13)$$

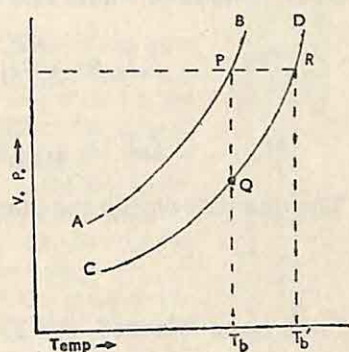


FIG. XI.4 Elevation of b. pt. of a solution

XI.7. Depression of Freezing Point of Solutions. The normal freezing point of a liquid is the temperature at which the liquid and the solid phases have the same vapour pressure, the system being maintained under one atmosphere. In Fig. XI.7, AB and AC are the vapour-pressure curves of liquid and solid phases of pure solvent. These intersect at A, which indicates the freezing temperature T_f of the pure solvent, the vapour pressure at A being p_1^0 .

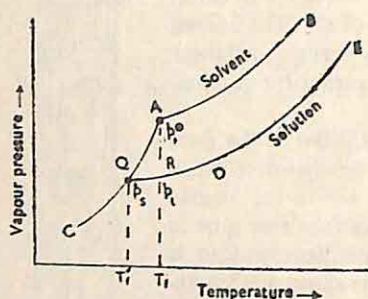


FIG. XI.7 Lowering of freezing point of a solution

than T_f . The freezing point is lowered due to the presence of the solute. It is necessary to emphasise here that the solid phase at Q must be that of the pure solvent and should not be a solid solution or a compound. A quantitative relation between the concentration of the solution and the freezing pt. depression can be worked out thermodynamically with the help of Raoult's law; the solution, being dilute, is considered as an ideal one.

The vapour-pressures at A and Q are p_1^0 and p_s and both of them lie on the vap-pressure curve of the solid phase. Using Clausius-Clapeyron equation,

$$(a) \ln p_1^0 = -\frac{L_s}{R} \cdot \frac{1}{T_f} + Z; \quad \text{and} \quad (b) \ln p_s = -\frac{L_s}{R} \cdot \frac{1}{T_f'} + Z$$

where L_s = molar latent heat of sublimation and Z a constant.

$$\therefore \ln \frac{p_s}{p_1^0} = -\frac{L_s}{R} \left[\frac{1}{T_f'} - \frac{1}{T_f} \right] = -\frac{L_s}{R} \cdot \frac{\Delta T}{T_f^2}, \quad \dots (A)$$

putting $T_f - T_f' = \Delta T$ and assuming $T_f T_f' \approx T_f^2$.

Again, the vapour-pressures at Q and at R are p_s and p_1 and both of them lie on the vapour-pressure curve of the solution. From Clausius-Clapeyron equation, we have,

$$(c) \ln p_s = -\frac{L_v}{R} \cdot \frac{1}{T_f'} + Z_1 \quad \text{and} \quad (d) \ln p_1 = -\frac{L_v}{R} \cdot \frac{1}{T_f} + Z_1$$

where Z_1 is a constant and L_v = molar latent heat of vaporisation.

$$\therefore \ln \frac{p_s}{p_1} = -\frac{L_v}{R} \left[\frac{1}{T_f'} - \frac{1}{T_f} \right] = -\frac{L_v}{R} \cdot \frac{\Delta T}{T_f^2} \quad \dots (B)$$

Subtracting (B) from (A),

$$\ln \frac{p_1}{p_1^0} = -\frac{\Delta T}{RT_f^2} [L_s - L_v] = -\frac{L_f}{RT_f^2} \Delta T$$

since the molar latent heat of fusion of the solvent $L_f = L_s - L_v$.

$$\text{Rewriting,} \quad \ln \left(1 - \frac{p_1^0 - p_1}{p_1^0} \right) = -\frac{L_f}{RT_f^2} \Delta T$$

As $\frac{p_1^0 - p_1}{p_1^0}$ is quite small, expanding the logarithmic series, we have,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{L_f}{RT_f^2} \Delta T$$

From Raoult's law the mol-fraction of the solute $x_2 = \frac{p_1^0 - p_1}{p_1^0}$, hence

$$\frac{L_f}{RT_f^2} \Delta T = x_2 \quad \text{or} \quad \Delta T = \frac{RT_f^2}{L_f} x_2 \quad \dots (XI.7)$$

That is, the depression in freezing point is proportional to the mol-fraction of the solute. This again is a colligative property.

In dilute solutions, mol-fraction $x_2 \approx \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1}$, when w_2 gms of solute are dissolved in w_1 gms of solvent. The mol-wts. of solute and solvent are M_2 and M_1 . Hence,

$$\Delta T = \frac{RT_f^2}{L_f} \cdot \frac{w_2 M_1}{w_1 M_2} = \frac{RT_f^2}{l_f} \cdot \frac{w_2}{w_1 M_2}$$

$$\therefore \Delta T = \frac{RT_f^2}{1000 \times l_f} \left[\frac{w_2 \times 1000}{w_1 M_2} \right] \quad \dots (XI.8)$$

$$\text{That is} \quad \Delta T = \frac{RT_f^2}{1000 \times l_f} m, \quad \dots (XI.9)$$

m , being the molality of the solution, equals $\frac{w_2 \times 1000}{w_1 \times M_2}$, where l_f is the latent heat of fusion per gm.

$$\text{We may then say,} \quad \Delta T = k_f m \quad \dots (XI.10)$$

where k_f is a constant for a given solvent equal to $\frac{RT_f^2}{1000 \times l_f}$. The constant k_f is called the *molal depression constant* or the *cryoscopic constant*.

When $m = 1$, $k_f = \Delta T$, i.e., the molal depression constant is equivalent to the depression of freezing point of a solution of unit molality. One molal solution would however be too concentrated to obey Raoult's law. The value of k_f is obtained either from equation (XI.10) using a dilute solution or computed from $RT_f^2/1000l_f$ for the solvent. Different solvents have their specific molal depression constants, some of which are given in the Table below. Some substances like camphor, pinene dibromide etc. have very high k_f values, which have found special applications.

TABLE : MOLAL DEPRESSION CONSTANTS

Solvent	m.pt. ($^{\circ}\text{C}$)	k_f	Solvent	m.pt. ($^{\circ}\text{C}$)	k_f
Water	0	1.86	Cyclohexane	6.5	20.2
Acetic acid	16.5	3.9	Naphthalene	80.2	7.0
Benzene	5.5	5.12	Camphor	—	40.0
Nitrobenzene	5.6	6.90	Pinene dibromide	—	81.0

XI.8. Measurement of Freezing Point Depression. (i) *Beckmann's Method.* A sketch of the apparatus used is given in Fig. XI.8. A wide glass tube 'A' with a side arm B is taken with a known weight of the liquid solvent. The tube is fitted with a cork through which are introduced a Beckmann thermometer *T* and a stirrer *S*₁. The tube A is placed in a much wider tube C, which serves as an air-jacket. The entire thing is then kept immersed in a freezing mixture. There is also a stirrer *S*₂ to stir the freezing mixture.

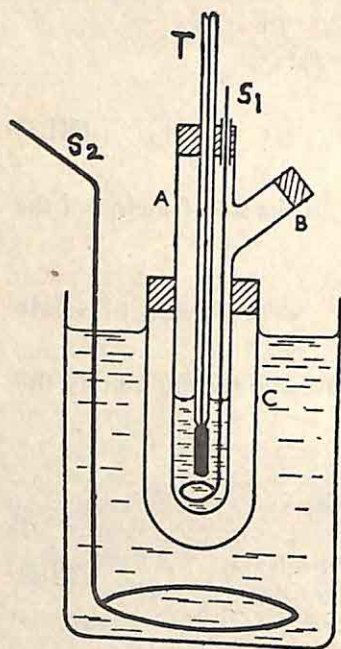


FIG. XI.8 Beckmann's method for measuring f. pt. depression

The tube A is first directly put in freezing mixture to solidify the solvent. The tube is then slowly warmed in hand with continuous stirring till fully melted. It is then placed in the air jacket C and surrounded by freezing mixture. The solvent is stirred slowly ; its temperature goes down steadily. The temperature actually goes somewhat below the freezing pt. due to unavoidable supercooling. But when the crystallisation just starts, the temperature jumps up and remains steady for a reasonable time. This steady temperature is recorded from the Beckmann thermometer. A weighed pellet of solute is next added to the solvent through side arm B. The freezing point of the solution is again recorded as before. The difference of the two readings in the Beckmann thermometer gives the depression of the freezing point of the solution.

(ii) *Rast's Method.* In this method camphor with its very high molal depression constant ($k_f = 40$) is used as solvent and as such the method is applicable to solutes like alkaloids which are soluble in molten camphor. Even for dilute solutions, the freezing point is considerably depressed and the lowering can be measured with ordinary thermometers. Usually the f-pt. of pure camphor is first determined and then a solute of known mol-wt. is added in known amounts to a definite wt. of camphor and melted. The mixture is cooled and powdered and subsequently freezing point is determined. From this, the value of molal freezing point constant is obtained.

Once k_f is known for the camphor sample, it can be mixed with a definite weight of a solute of unknown mol-wt. and the freezing point determined by repeated melting and freezing. The mol-wt. of the solute can then be calculated from equation (XI.8).

In this method other 'solvents' with high molal freezing constants are also used such as Borneol hexachloro ethane, tetrabromo-methane, camphor, quinone etc. These solvents are solids at room temperature, the melting points of solvents or their solutions can be easily determined by the usual capillary method and very little quantity of substance is needed.

XI.9. Osmosis. It is common knowledge that when a solution is brought in contact with pure solvent, diffusion occurs. For example, if water is poured carefully through a narrow tube on a saturated aqueous copper sulphate solution in a test tube, the two layers are well defined. On standing the two layers begin to merge ; copper sulphate diffuses into the water layer and water into the blue copper sulphate solution. The process of diffusion continues until the concentration is uniform throughout. Nature tends to attain equilibrium by diffusion. The rate of diffusion is found to be proportional to the concentration of the solution used and the rate also increases with rise in temperature. When two solutions of unequal concentration are placed together similar diffusion occurs until equality of concentration is achieved.

There are membranes which are impervious to solute molecules but they allow the solvent molecules to pass through them. These are called *semipermeable membranes*. Many such semipermeable membranes occur in nature while many others are artificially prepared. The animal bladders such as pig's bladder, intestinal walls, skins of potatoes and other plants, the inner walls of egg-shells etc. serve as semipermeable membranes. Parchment paper, gelatine, cellophane films, layers of precipitated copper ferrocyanide on porous walls are also good semipermeable membranes : these permit solvent molecules to pass through but not the solute.

Now if a solution and pure solvent be kept separated by means of a semipermeable membrane, the solvent molecules only will pass through the membrane into the solution in order to dilute it. *This phenomenon of diffusion of a solvent through a semipermeable membrane from the solvent to a solution or from a dilute solution to a concentrated one is called osmosis.* Since the solute cannot diffuse through the membrane, nature tends to achieve equilibrium through osmosis. It is understood that the passage of solvent occurs in both directions, but the diffusion of the solvent from the solvent to the solution is much more rapid than that in the opposite direction.

In 1784 Abbe' Nollet made the first striking observation that when a pig's bladder filled with alcohol and tied at the neck was kept immersed in water, it swelled and swelled and ultimately burst. A still better demonstration was to stretch and tie a piece of bladder across the mouth of an inverted thistle funnel. It was filled with concentrated cane sugar solution and kept partly immersed in water as in Fig. XI.9. The liquid inside the stem of the funnel rose up gradually and finally the level became stationary. This is because due to osmosis, the water from outside enters through the membrane but when the hydrostatic pressure inside counterbalanced the force which caused the water to diffuse from outside, the eqm. is attained, and the level becomes stationary. The bladder in this experiment may be conveniently replaced by a cellophane.

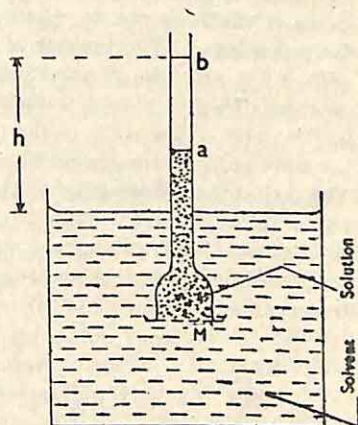


FIG. XI.9 Osmosis and osmotic pressure

Other illustrations of osmosis may be cited. When a dry prune is placed in water, it swells as water enters through the semipermeable skin of the fruit due to osmosis. The hard outer shell of an egg may be removed by dissolving in dil. HCl. If the egg is then placed in water, it swells. On the other hand, if the egg is placed in very concentrated solution of salt, it will shrink. The thin membrane beneath the hard shell is semipermeable.

Red blood corpuscles when placed in a strong solution are found to shrivel when observed under microscope. But they swell and burst when kept in a weak solution, which is the cause for *haemolysis*.

XI.10. Osmotic Pressure. In the experiment with sugar solution in the thistle funnel (Fig. XI.9) it is found that the hydrostatic pressure is built up and when it reaches a certain magnitude osmosis ceases. The diffusion of solvent through the membrane does not end, but the rates of diffusion in both directions become the same. The magnitude of the pressure ($h\rho g$ here) which prevents osmosis is called the osmotic pressure. This may be clearly understood in the following way.

Suppose we have a U-tube, as in Fig. XI.10, provided with a semipermeable partition at the centre X.

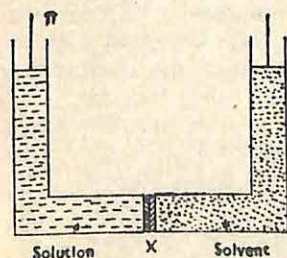


FIG. XI.10 Osmotic pressure

One arm of the tube is filled with a solution and the other with pure solvent. There are piston arrangements for applying pressures on the liquids. Normally solvent will pass through X into the solution i.e., osmosis will occur. This diffusion of the solvent into the solution through the membrane can be counteracted by applying pressure π over the solution. The excess pressure π on the solution that would just prevent osmosis is called the osmotic pressure of the solution. The term is somewhat misleading, for a solution by itself cannot exert any pressure due to osmosis. *The osmotic pressure of a solution is the pressure required to prevent osmosis when the solution is separated from pure solvent by a semipermeable membrane.*

We shall see later that the magnitude of the osmotic pressure depends on various factors. This pressure is however not dependent on the nature of the membrane provided it is really a semipermeable one. Hence although the membrane makes the osmotic pressure manifest, it is not the cause for the existence of the osmotic pressure. The latter should be considered as a measure of difference in the thermodynamic potentials of the solvent and the solution.

XI.11. Experimental Measurement of Osmotic Pressure. Two main difficulties arise in the experimental measurement of the osmotic pressure of a solution. Firstly, to prepare a satisfactory semipermeable membrane which would stand fairly high pressures is not so easy. Secondly, the application and measurement of high pressures involved very often proves also a difficult problem.

One of the extensively used semipermeable membrane is prepared by Traube's method by depositing a ppt. of copper ferrocyanide in the pores of an earthenware pot. And earthenware porous pot, specially prepared without binders, is thoroughly cleaned, dried and finally soaked in water till the pores are filled with water. The pot is then placed in a 3% solution of CuSO_4 for a few hours. The interior of the pot is then washed and quickly dried. Next it is filled up with a 3% solution of potassium ferrocyanide and the pot is again placed in copper sulphate solution. The diffusion of the salts leads to a deposit of jelly-like precipitate of copper ferrocyanide in the pores of the walls of the pot. In fact a membrane is formed inside the pores turning the pot into a cell of semipermeable walls. Sufficient time is allowed for any diffusion of salt to cease. The cell is then thoroughly washed free from all electrolytes and is ready for measurement. In 1877, Pfeffer made the successful quantitative determination of osmotic pressure. His method is still followed with, of course, considerable modification and improvement.

Pfeffer's Method. A semipermeable cell *A*, an earthenware porous pot with deposit of copper ferrocyanide, is cemented with a wide glass tube *B*. The tube *B* has a side-tube to which is attached a calibrated manometer (*M*) with N_2 -gas enclosed above mercury. A diagrammatic sketch of the apparatus is given in Fig. XI.11. The cell and the space up to mercury is filled up with the solution. The filling is made through a tube which is ultimately sealed off. The pot is placed in a bath of pure solvent at a constant temperature. As the solvent diffuses in, the pressure rises. When equilibrium is attained, the pressure is recorded from the manometer. The concentration of the solution may change to some extent due to entry of solvent but with a closed type manometer the dilution is indeed negligible.

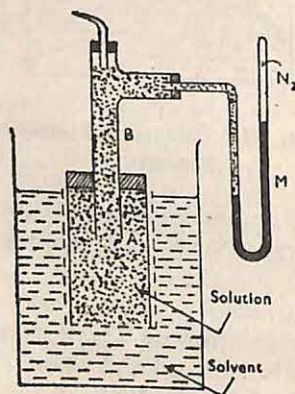


FIG. XI.11 Det. of osmotic pressure

the system such that copper ions travel outwards and ferrocyanide ions travel inwards. These ions encounter each other at the porous wall where a thin and uniform deposit of copper ferrocyanide was formed. This proved to be a more efficient semipermeable membrane capable of withstanding much higher pressure. Subsequently other workers also introduced modifications in measurement of pressure. Instead of using a manometer, the pressure was measured with the help of an electric resistance gauge, or by a water interferometer from which the pressure was obtained from the change in refractive index of water.

Berkeley and Hartley's Method. Berkeley and Hartley (1906) introduced a different technique in measuring osmotic pressure. In this method the solvent is not allowed to enter the solution but an external pressure is applied on the solution just enough to prevent inflow of solvent. This applied pressure is the osmotic pressure. An outline of the apparatus is shown diagrammatically in Fig. XI.12.

The inner porcelain tube has electrically deposited

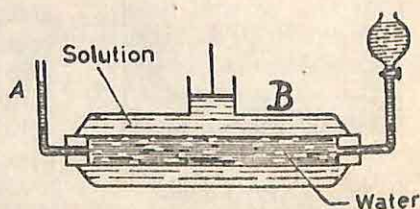


FIG. XI.12 Det. of osmotic pressure (Berkeley and Hartley)

copper ferrocyanide in the pores of its wall and serves as the semipermeable membrane. At one end of the tube is fitted a capillary tube *A* and at the other end there is a tube leading to a funnel through a stop cock. A much wider gun-metal tube *B* surrounds the inner tube and is tightly cemented to it. *B* is provided with a piston to which a pressure gauge is attached. The annular space between the two tubes is filled up with the solution, while inside the inner tube is introduced pure solvent up to a definite mark *A* in the capillary. A pressure is applied on the piston so that the water level in the capillary remains constant. This pressure recorded from the gauge is the osmotic pressure. The advantage of the method lies in its rapidity of determination and that the concentration of the solution remains unaltered.

Comparison of Osmotic Pressures. De Vries developed an ingenious method for comparison of osmotic pressure of two solutions using plant cells for the purpose. The walls of plant or animal cells with their inner membrane behave as semipermeable membranes. These permit water to diffuse through them but do not allow the substances of the cell-sap such as sugar, salts etc. to come out. When such a cell is placed in a concentrated solution, the water of the cell passes outwards and the membrane of the cell wall shrinks; this is called *plasmolysis*. On the other hand, if the cell is placed in a dilute solution or in water, it swells. The shrinking or swelling can be clearly detected by observing them under the microscope, especially if the cells are stained.

The osmotic pressures of the two solutions were compared by finding out how much these had to be diluted to produce no effect—i.e., no shrinking or swelling—on the cells. Such solutions which have no effect on the cell fluid are called “*isotonic*” solutions; these are in equilibrium with the cell-sap so far as their tensions are concerned. A 0.84 per cent NaCl solution is isotonic with the contents of our red blood cells and is usually called “*normal saline*”. Had the cell-membrane be perfectly semipermeable, isotonic solutions would also be isosmotic, that is, the two solutions would also have same osmotic pressure. The imperfect semipermeability of the cell-membranes means that isotonic solutions are not strictly isosmotic.

Different explanations have been forwarded from time to time for the semipermeable nature of the membranes. The early idea that the pores of the membrane were not sufficiently big to permit the solute molecules to pass was discarded for the simple fact that the membranes were also impervious to solute molecules which were definitely known to be smaller in dimensions compared to the solvent molecules. In other theories, the solvent molecules are supposed to be soluble in the membrane material, or to form loose compounds with the membrane molecule or adsorbed in the capillaries of the membrane. It is yet difficult to say very definitely anything regarding the mechanism of semipermeability. The solution has a lower vapour pressure than that of the pure solvent and the process of the solvent passing into the solution involves probably the distillation through the capillaries of the membrane.

XI.12. Laws of Osmotic Pressure. The wealth of data which accumulated from the experiments of Pfeffer, of Morse and Frazer, of Berkeley and Hartley and their co-workers led to certain very interesting conclusions. It was realised quite early that the osmotic pressure of solutions depends upon both the temperature and the concentration of the solutions. Quantitatively these were formulated into the following laws.

Law 1. *Temperature remaining constant, the osmotic pressure (π) of a solution is directly proportional to its concentration (C).*

That is, $\pi = k_1 C$, where k_1 is a constant,

The concentration C is expressed in molar units, so that $C = 1/V$ when 1 gm-mole of the solute is present in V litres of solution.

Hence $\pi V = k_1 \dots$ (XI.11)

It was van't Hoff who pointed out this fact that osmotic pressure obeys a law analogous to that of gas-pressure, i.e., Boyle's Law.

Law 2. *Concentration remaining constant, the osmotic pressure (π) of a solution varies directly as the absolute temperature (T).*

That is $\pi = k_2 T$, k_2 is a constant

It is important to note that this effect of temperature on the osmotic pressure is similar to the effect of temperature on gas pressure, as enunciated in Charles's law.

Below are appended some experimental data which establish the validity of the two laws.

TABLE : OSMOTIC PRESSURE OF SUCROSE SOLUTIONS (15°C)

Conc. in gms per 100 gms	π (osmotic pressure) mm of Hg	π/C
10	535	535
20	1016	508
40	2082	521
60	3075	513

TABLE : OSMOTIC PRESSURE OF SUCROSE SOLUTIONS (0.1 molal)

Temp. (T°K)	π (osmotic pressure)	$\pi/T (\times 10^3)$
273	7.085	2.594
283	7.334	2.591
293	7.605	2.595
298	7.729	2.594

The two laws enunciated above may be combined, so as to give the relation

$$\pi = CKT,$$

when both temperature and concentration would vary. K is a constant. If the solution contains n gm-moles of solute in V litres of solution, we have

$$\pi = \frac{n}{V} KT \quad \text{or} \quad \pi V = nKT. \quad \dots (XI.13)$$

It may then be stated : "*Equimolecular quantities of different solutes dissolved in the same volume of a solvent exert equal osmotic pressure at the same temperature.*" It is presumed that the solutes are supposed not to suffer dissociation or association in the solution. This is sometimes mentioned as the third law for osmotic pressures.

As equimolecular quantities contain the same number of molecules, the above statement may be expressed alternatively : "Equal volumes of different solutions which are at the same temperature and exert same osmotic pressure contain an equal number of solute molecules." This is indeed Avogadro's law applied to solutions. The osmotic pressure is thus dependent on the number of molecules and independent of their nature. So it is a colligative property.

The remarkable identity of equation (XI.13) with the ideal gas equation was pointed out by van't Hoff.

Ideal gas equation : $PV = nRT$

Osmotic pressure equation : $\pi V = nKT$

When the experimental values of π were substituted in equation XI.13, the numerical value of K was found to be 0.082 litre atmosphere/degree, the same as that of " R " of the gas equation. Equation XI.13 for solutions now becomes, (C is the molar concentration of the solute in the solution),

$$\left. \begin{array}{l} \pi V = nRT \\ \text{or} \quad \pi = CRT \end{array} \right\} \quad \dots (XI.14)$$

Van't Hoff therefore rightly stated : "*The osmotic pressure of a substance in solution is the same as it would exert if it existed as a gas in the same volume as that occupied by the solution at the same temperature.*" The solution is dilute and the volume occupied by the solute in solution is negligible compared to the volume of the solution.

This is generally called van't Hoff's law of osmotic pressure, which is really a combination of the separate laws stated earlier.

XI.13. Thermodynamic Derivation of the Osmotic Pressure Law. Suppose a large reservoir of pure solvent having vapour pressure p_1^0 is placed by the side of another reservoir containing a solution having a vapour pressure p_1 . It is known $p_1^0 > p_1$.

Let Δx gm-mole of the pure solvent be vaporised at constant temperature (T) by keeping the pressure infinitesimally smaller than p_1^0 . Since the process is carried out reversibly at constant pressure and temperature, the Gibbs potential change

$$\Delta G_1 = vdp - sdT = 0$$

Next the Δx gm-moles of solvent vapour at pressure p_1^0 is placed in a cylinder with a piston and expanded reversibly and isothermally until the pressure falls to p_1 . The Gibbs potential change, $\Delta G_2 = \Delta x RT \ln \frac{p_1}{p_1^0}$

Finally, the vapour, Δx gm-moles at pressure p_1 , is condensed reversibly and isothermally to the reservoir of solution. The Gibbs potential change, for the isothermal isobaric condensation, $\Delta G_3 = 0$.

Hence, the net Gibbs potential change in the process of dilution of the solution by Δx gm-moles of solvent is

$$\Delta G = \Delta x RT \ln \frac{p_1}{p_1^0} \quad \dots (XI.15)$$

The change in concentration due to this dilution is negligible. Δx gm-mole is too small in comparison to the solution in the large reservoir.

The dilution of the solution can also be effected in other ways and the Gibbs potential change would be the same provided the processes are reversible. Suppose the solution is kept separated from the solvent by a semipermeable membrane. Let the pressure on the solution be P and that on the solvent P' , so that diffusion of solvent through the membrane is just prevented. Then the osmotic pressure (π) of the solution is $P - P'$.

By lowering of the pressure on the solution, allow Δx gm-moles of pure solvent pass into the solution reversibly and isothermally. If $\bar{V}$ is the partial molar volume of the liquid solvent, then the volume entering the solution is $\Delta x \bar{V}$. The Gibbs potential change

$$\Delta G = \int_P^{P'} \Delta x \bar{V} dP = \Delta x \bar{V} (P' - P) = -\Delta x \bar{V} \pi \quad \dots (XI.16)$$

assuming $\bar{V}$ to remain constant.

Both the equation XI.15 and XI.16 represent the Gibbs potential change for the addition of same amount of solvent to the same solution, then

$$-\Delta x \bar{V} \pi = \Delta x RT \ln \frac{p_1}{p_1^0} = -\Delta x RT \ln \frac{p_1^0}{p_1}$$

$$\text{or} \quad \pi \bar{V} = RT \ln \frac{p_1^0}{p_1} \quad \dots (XI.17)$$

This is the thermodynamic relation between osmotic pressure and vapour pressure.

Very dilute solutions of non-volatile non-electrolytes may be regarded as ideal and Raoult's law holds good, so that

$$p_1 = x_1 p_1^0, \text{ where } x_1 \text{ is the mol-fraction of the solvent.}$$

$$\text{i.e.,} \quad \ln \frac{p_1^0}{p_1} = -\ln x_1 = -\ln (1 - x_2) \approx x_2$$

where mol-fraction of the solute (x_2) is quite small and $\ln (1 - x_2) \approx -x_2$. Substituting in eqn. (XI.17), we have,

$$\pi \bar{V} = RT x_2 \quad \dots (XI.18)$$

$$\text{or} \quad \pi \bar{V} = \frac{n_2}{n_1 + n_2} RT$$

Since in dilute solution $n_1 \gg n_2$; $\therefore \pi \bar{V} = \frac{n_2}{n_1} RT$

Where n_2 gm moles of solute are dissolved in n_1 gm-moles of solvent, the volume of the latter is, say, $v = n_1 \bar{V}$.

$$\therefore \pi v = n_2 RT \quad \dots (XI.19)$$

$$\text{or} \quad \pi = \frac{n_2}{v} RT = CRT \quad \dots (XI.14)$$

where C is the molar concentration of the solution. This is the same relation proposed earlier.

XI.14. Osmotic Pressure and Other Colligative Properties. Rewriting equation (XI.18);

$$x_2 = \frac{\pi \bar{V}}{RT} = \frac{\pi M_1}{\rho RT} \quad \dots (XI.20)$$

(where M_1 = mol. wt. and ρ = density of the solvent.)

$$\text{From Raoult's law we know, } x_2 = \frac{\Delta p}{p_1^0},$$

$$\text{hence} \quad \frac{\Delta p}{p_1^0} = \frac{\pi M_1}{\rho RT} \quad \dots (XI.21)$$

This gives the relation between osmotic pressure and relative lowering of vap-pressure.

Further, we know from equation (XI.3) that the elevation of boiling point of a solvent is proportional to the mol-fraction of the solute,

$$x_2 = \frac{L_v}{RT_b^2} \cdot \Delta T$$

Substituting this in equation (XI.20), we find,

$$\frac{L_v}{RT_b^2} \cdot \Delta T = \frac{\pi M_1}{\rho RT}$$

$$\text{Or} \quad \pi = \frac{\rho T}{T_b^2} \cdot \frac{L_v}{M_1} \cdot \Delta T$$

$$\therefore \frac{L_v}{M_1} = l_v, \quad \pi = \frac{\rho T}{T_b^2} \cdot l_v \Delta T \quad \dots (XI.22)$$

$$\text{i.e., using eqn. (XI.5),} \quad \pi = \frac{\rho RT \cdot \Delta T}{1000 \times K_b} \quad \dots (XI.22a)$$

where T is the temperature at which osmotic pressure π is measured.

Similarly for the depression of freezing point (equation XI.7),

$$x_2 = \frac{L_f}{RT_f^2} \Delta T$$

Combining with equation (XI.20), we have

$$\pi = \frac{\rho L_f T}{M_1 T_f^2} \cdot \Delta T = \frac{\rho T l_f}{T_f^2} \cdot \Delta T \quad \dots (XI.23)$$

$$\text{i.e., from eqn. (XI.10), } \pi = \frac{\rho RT}{1000 \times K_f} \Delta T \quad \dots (XI.23a)$$

The osmotic pressure is therefore directly related to other colligative properties.

XI.15. Determination of Molecular Weights from Colligative Properties of Solutions. The colligative properties of solutions are extensively employed for molecular

weight determination, especially the depression of freezing pt. and the elevation of boiling point. If we have a solution of w_2 gms of solute of unknown mol. wt. M_2 dissolved in w_1 gms of a given solvent (mol. wt. M_1), the different colligative properties are quantitatively expressed as :

- I. Lowering of vapour pressure (eqn. XI.2) : $\frac{\Delta p}{p_1^0} = \frac{n_2}{n_1 + n_2} = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2}$
- II. Boiling pt. elevation (eqn. XI.4) : $\Delta T = K_b \cdot \frac{w_2 \times 1000}{w_1 \times M_2}$
- III. Freezing pt. depression (eqn. XI.8) : $\Delta T = K_f \cdot \frac{w_2 \times 1000}{w_1 \times M_2}$
- IV. Osmotic pressure (eqn. XI.14) : $\pi = CRT = \frac{w_2/M_2}{v} RT$

We have further seen that the extent of lowering of vapour pressure, or depression of f.pt. or elevation of b.pt. can be measured with reasonable accuracy. Thus, with the help of such a measurement and application of the relevant equation from above, the molecular weight (M_2) of the solute is found out easily. A few problems are worked out below to illustrate such determination.

[In the problems cited below 'a' gms of solute are present in 'b' gms of solvent.]

Problem 1. The melting point of phenol is 40°C . A solution containing 0.172 gms acetanilide ($\text{C}_8\text{H}_9\text{ON}$) in 12.54 gms phenol freezes at 39.25°C . Calculate the freezing point constant and the latent heat of fusion of phenol.

The freezing point depression, $\Delta T = 40 - 39.25 = 0.75$; mol wt. $M_2 = 135$

$$\text{Hence, } K_f = \frac{\Delta T \cdot b \cdot M_2}{a \times 1000} = \frac{0.75 \times 12.54 \times 135}{0.172 \times 1000} = 7.38$$

$$\text{Since } K_f = \frac{RT_f^2}{l \times 1000} = \frac{2 \times (313)^2}{l \times 1000}$$

$$\text{or, latent heat of fusion of phenol, } l = \frac{2 \times 313^2}{7.38 \times 1000} = 26.5 \text{ calories per gm.}$$

Problem 2. The freezing point of pure benzene = 5.44°C and that of a solution containing 2.092 gms of benzaldehyde in 100 gms of benzene is 4.44°C . Calculate the mol-weight of benzaldehyde, when K_f for benzene is 5.1.

$$\Delta T_f = \frac{a \times 100}{b \times M_2} \cdot K_f$$

$$\text{or } M_2 = \frac{a \times 1000}{b \times \Delta T_f} \cdot K_f = \frac{2.092 \times 1000}{100 \times (5.44 - 4.44)} \times 5.1 = 106.6.$$

Problem 3. A solution containing 2.423 gms of sulphur in 100 gms of naphthalene (m. pt. 80.1°C) gave a freezing point depression of 0.64°C . The latent heat of fusion of naphthalene is 35.7 calories per gm. What is the molecular formula of sulphur in the solution?

$$\Delta T_f = \frac{RT_f^2}{1000 \cdot l} \cdot \frac{a \times 1000}{b \times M_2}$$

$$\text{or } 0.64 = \frac{2 \times (353.1)^2}{1000 \times 35.7} \cdot \frac{2.423 \times 1000}{100 \times M_2}$$

$$\text{whence, } M_2 = 264$$

But atomic weight of sulphur is 32. So, mol-formula of sulphur is S_8 .

Problem 4. The boiling point of acetic acid is 118.1°C and its latent heat of evaporation is 121 cal. per gm. A solution containing 0.4344 gms anthracene in 44.16 gms of acetic acid boils at 118.24°C . What is the mol-weight of anthracene?

$$\Delta T_b = 0.14^\circ,$$

$$M_2 = K_b \frac{a \times 1000}{b \times \Delta T_b} = \frac{RT_b^2}{l \times 1000} \cdot \frac{a \times 1000}{b \times \Delta T_b}$$

$$= \frac{.002 \times (391.1)^2}{121} \cdot \frac{0.4344 \times 1000}{44.16 \times 0.14} = 178$$

Problem 5. At 25°C , the vapour-pressure of water is 23.55 mm, what would be the vapour pressure of a solution containing 6 gms of urea (mol-weight 60) in 100 gms of water at the same temperature.

Let P be the vapour pressure of the solution. Then

$$\frac{P_0 - P}{P_0} = \frac{n_2}{n_2 + n_1}$$

or
$$\frac{23.55 - P}{23.55} = \frac{6/60}{6/60 + 100/18} = \frac{0.1}{0.1 + 5.55}$$

whence

$$P = 23.13 \text{ mm.}$$

Problem 6. A current of dry air is passed through a series of bulbs containing a solution of 8.914 gms of nitrobenzene in 100 gms of alcohol and then through a series of bulbs containing pure alcohol, at the same temperature. After the passage of air, the loss in weight of bulbs containing the solution was 2.034 gms and that of the bulbs of pure alcohol was 0.0685 gms. Calculate the mol-weight of nitrobenzene.

Let P and P_0 be the vapour pressures of alcohol over the solution and the pure solvent at that temperature. The solute is regarded as non-volatile.

On passing through the solutions, the air was saturated up to the pressure P , by vaporising 2.034 gms of alcohol. Subsequently, the air was led through pure solvent and it was saturated to pressure P_0 , for which it absorbed a further quantity of alcohol vapour, i.e., 0.0685 gms. Hence the total amount of vapour required to saturate the same volume of air up to pressure $P_0 = 2.034 + 0.0685 = 2.1025$ gm.

Obviously, $P \propto 2.034$; and $P_0 \propto 2.1025$.

Hence
$$\frac{P_0 - P}{P_0} = \frac{0.0685}{2.1025}$$

But
$$\frac{P_0 - P}{P_0} = \frac{n_2}{n_1} = \frac{\frac{8.914}{M_2}}{\frac{100}{46}} = \frac{8.914 \times 46}{100 \times M_2}; \text{ (mol. wt. of alcohol} = 46)$$

or
$$\frac{0.0685}{2.1025} = \frac{8.914 \times 46}{100 \times M_2}$$

whence,

$$M_2 = 125.8$$

Problem 7. At 100°C the vapour pressure of a solution of 6.5 gms of a solute in 100 gms dilute solution. What is the boiling point of the solution? ($K_b = 0.52$). Assume the laws of

At 100°C , the vapour pressure of pure water $P_0 = 760$ mm.

So
$$\Delta P = P_0 - P = 760 - 732 = 28 \text{ mm.}$$

Hence,
$$\frac{n_2}{n_1} = \frac{\Delta P}{P_0} = \frac{28}{760}$$

Now,
$$\Delta T_b = K_b \frac{a \times 1000}{b \times M_2}$$

(Since $\frac{a}{M_2} = n_2$, and $b = n_1 M_1$)
$$= K_b \cdot \frac{n_2}{n_1} \cdot \frac{1000}{M_1} = 0.52 \times \frac{28}{760} \times \frac{1000}{18} = 1.064^\circ$$

Hence the boiling temperature of the solution, $T = 100 + 1.064 = 101.064^\circ\text{C}$.

Problem 8. Calculate the freezing point of a solution of cane sugar which has an osmotic pressure of 5 atmospheres at 50°C.

From equation (XI.23a),
$$\pi = \frac{\rho RT \cdot \Delta T}{1000 \times K_f} = \frac{1 \times 0.082 \times 323 \times \Delta T}{1.86}$$

or
$$\Delta T = \frac{5 \times 1.86}{0.082 \times 323} = 0.352, \text{ using } R \text{ in c.c. atmos, as } \rho \text{ is in c.c.}$$

The freezing pt. of the solution is -0.352°C .

XI.16. Abnormal Behaviour of Solutions. Experimental measurements of osmotic pressure, vapour-pressure lowering, freezing point depression or boiling point elevation readily conform to the values expected from the relations derived in the preceding sections, especially when dilute solutions of non-electrolytes are taken. In fact, b.pt. elevation or f.pt. depression are often employed for determination of molecular weights. But there are instances when the experimental results are at variance with the theoretically calculated values. The abnormal values obtained may be attributed to two different causes.

I. The real solutions, even of non-volatile non-electrolytes, often are not ideal, especially at higher concentrations. This non-ideal behaviour of solutions lead to abnormal results.

II. Abnormal experimental results are also obtained when the solutes, even in dilute solution, are either associated or dissociated. We may consider these separately.

Non-ideality in Solution. All the laws for dilute solutions are derived on the basis of Raoult's law. Raoult's law is valid for ideal solutions only. But real solutions obey Raoult's law only at low concentrations. When the concentration is high, solutions indeed exhibit considerable departure from the law. The deviations may be positive or negative. This is illustrated in Fig. XI.13, in which vapour pressures are plotted against concentrations (mol-fraction) of the solvent ($p_1 = x_1 p_1^\circ$). In this figure, Curve I is the linear one as theoretically expected from the Raoult's law, while curves II and III are the typical experimental observation with positive and negative deviations from the law. At low concentrations of the solute however, all the three curves merge together. This means that at high dilutions, all solutions approach ideality. This is why the colligative properties of *dilute solutions* are observed to obey the relations deduced earlier satisfactorily.

The element of non-ideality enters into the picture when the molecules of the solute and the solvent affect each others' intermolecular forces, or if there be association or complex formation between the solute and the solvent. These become quite conspicuous when the concentration of the solution is high. Hence at higher concentration the experimental results are found to be abnormal.

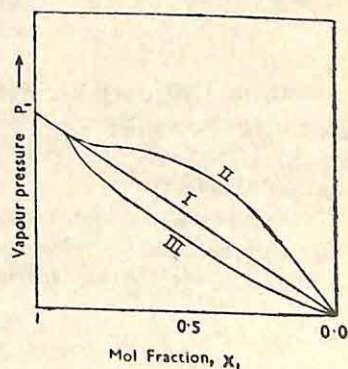


FIG. XI.13 Raoult's law and its deviations.

Association in Solution. Some solutes when dissolved in non-hydroxylic solvents like benzene, cyclohexane, carbon-tetrachloride, nitrobenzene etc. remain associated. Thus, carboxylic acids like acetic acid, benzoic acid etc. remain mostly as dimers in benzene solution. Evidence of the existence of association has also been found in the results of partition coefficient experiments (sec. X.3). The association would render the number of solute particles less than what it would have been if the solute were present as single molecules. The properties of dilute solutions, being colligative in nature, depend on the number of solute particles and not on their chemical composition. In consequence, the values of osmotic pressure, freezing point depression, boiling point elevation etc. would be less than those theoretically anticipated from the relations derived for them. The

molecular weight calculated from the observed freezing point lowering or boiling point elevation etc. in such cases would obviously be higher. The observed values for the mol. wt. of acetic acid obtained from freezing point depression are given in the table here, which shows that except in very dilute solutions, the molecular weight is nearly double that of its chemical formula (mol. wt. 60).

TABLE : OBSERVED MOL. WT. OF ACETIC ACID IN BENZENE SOLUTION

Molality	$\Delta T_f (^{\circ}\text{C})$	Obs. mol. wt.	Degree of Association
0.003	0.016	65.8	1.09
0.015	0.054	84.5	1.41
0.097	0.254	117.0	1.95
0.510	1.252	114.5	2.07
1.025	2.410	130.2	2.17

It is clear that at very high dilutions only acetic acid remains as single molecules in benzene solutions ; at low dilutions most of the acid remain as dimers. At fairly high concentration, the degree of association even exceeds 2. This is due to the fact that apart from association, the solution also shows positive deviation from Raoult's law to some extent.

The degree of association can also be evaluated. Suppose α is the degree of association i.e., the fraction of total solute present as dimers of mol. wt. $2M_0$. Then $(1-\alpha)$ fraction would remain as single molecules of mol. wt. M_0 . If M is the mean (observed) mol. wt., then

$$M \left(1 - \frac{\alpha}{2} \right) = 2M_0 \left(\frac{\alpha}{2} \right) + M_0 (1 - \alpha)$$

or

$$\alpha = \frac{2(M - M_0)}{M} \quad \dots (XI.24)$$

If n molecules are associated, instead of 2, the degree of association would similarly be given by,

$$\alpha = \frac{n(M - M_0)}{M(n - 1)} \quad \dots (XI.25)$$

With hydroxylic solvents like water, alcohols etc. carboxylic acids remain as single molecules and their mol. wts. are found to correspond to simple molecules. These solvents with high dielectric constants are often mentioned as dissociating solvents.

The finding of a higher value for mol.-wt. from a colligative property does not necessarily mean association of the solute molecules in solution. This may be illustrated in the case of nitrobenzene or in cyclohexane solution.

TABLE : OBSERVED MOL. WT. OF NITROBENZENE IN BENZENE SOLUTION

$(M_{\text{theoretical}} = 123)$							
Molar Conc.	$\Delta T_f (^{\circ}\text{C})$	M_{obs}	$\frac{M_{\text{obs}}}{M_{\text{theo}}}$	Molar Conc.	$\Delta T_f (^{\circ}\text{C})$	M_{obs}	$\frac{M_{\text{obs}}}{M_{\text{theo}}}$
0.286	1.632	129.7	1.06	0.735	3.950	143.7	1.15
0.496	2.720	137.0	1.11	1.180	6.230	152.7	1.35

The observed mol. wt. increases with higher and higher concentrations and does not tend to reach a constant value. There is also no other evidence or indication pointing towards association of nitrobenzene molecules in solution. It is very likely that the deviations from the normal value are due to the non-ideality of the solution arising out of the difference of intermolecular forces in each of solute and solvent.

Abnormal molecular weights are also found for phenols, alcohols, etc. when dissolved in benzene and other non-polar solvents. The higher values, it is believed, are partly due to association of solute molecules and partly due to non-ideality of the solutions.

Dissociation in Solution. In 1885, van't Hoff found that dilute aqueous solutions of electrolytes such as NaCl, MgSO₄ etc. show a considerable departure from the ideal. The observed osmotic pressure of solutions of salts of known concentration (C) was found to be much higher than that predicted from the relation, $\pi = CRT$. As a result the mol. wts. calculated from the observed osmotic pressure is much less than that from the chemical formula of the solute. Van't Hoff did not offer any explanation for the abnormal results, but introduced a factor, i , to contain the deviations from ideal equation in case of solutions of electrolytes, expressing

$$\pi_{ideal} = CRT, \quad \pi_{observed} = iCRT \quad \dots (XI.26)$$

Therefore,
$$i = \frac{\pi_{obs}}{\pi_{theo}} \quad \dots (XI.27)$$

The *van't Hoff's factor* " i " is thus the ratio of the observed osmotic pressure and the ideal osmotic pressure.

It was further found that for a given solution of an electrolyte the deviation in any colligative property would be the same as that in osmotic pressure, i.e.,

$$i = \frac{\pi_{obs}}{\pi_{theo}} = \frac{\Delta T_{f(obs)}}{\Delta T_{f(theo)}} = \frac{\Delta T_{b(obs)}}{\Delta T_{b(theo)}} = \frac{\Delta p_{obs}}{\Delta p_{(theo)}} \quad \dots (XI.28)$$

In high dilutions, " i " tends to the numerical value "two" for electrolytes like NaCl, MgSO₄, HNO₃, etc. For electrolytes like H₂SO₄, CoCl₂ etc. the value approaches "three"; for K₃Fe(CN)₆, the value tends to "four" and so on.

TABLE : VAN'T HOFF FACTOR " i " FROM OBS. ΔT_f , FOR DIFFERENT ELECTROLYTES

Electrolyte	Molality			
	1.00	0.1	0.01	0.001
NaCl	1.81	1.87	1.94	1.97
HCl	2.12	1.89	1.94	1.98
CuSO ₄	0.93	1.12	1.45	—
HNO ₃	1.92	1.89	1.96	1.97
H ₂ SO ₄	2.17	2.12	2.46	2.82
CoCl ₂	—	2.62	2.75	2.90
Pb(NO ₃) ₂	1.31	2.13	2.63	2.89
K ₃ Fe(CN) ₆	—	2.85	3.36	3.82

The explanation of the abnormal colligative properties of solutions of electrolytes comes readily from the Arrhenius dissociation theory. According to the dissociation theory, the electrolyte molecules in solution break up into positive and negative ions. In very high dilutions, the dissociation is complete. Thus in dilute solutions, p molecules of NaCl will give rise to $2p$ ions; p molecules of H₂SO₄ will give $3p$ ions and so on. Since the colligative properties depend on the units of solute present in solution irrespective of their chemical nature and because, due to ionisation the number increases, the values of the colligative properties observed are much higher. In fact, these results from the dilute solutions gave the strongest and most dramatic support to the Arrhenius theory of dissociation.

Generally speaking, suppose a molecule breaks up into n ions in a given solution of concentration c . If α is the degree of dissociation, then

$$\text{conc. of undissociated molecules} = (1 - \alpha)c$$

$$\text{and conc. of (dissociated) ions} = n \cdot \alpha c$$

$$\text{Hence total conc. of solute particles} = c[1 + n - 1\alpha]$$

The osmotic pressure of such a solution, $\pi_{obs} = c[1+(n-1)\alpha]RT$. But from eqn. (XI.28) van't Hoff's corrected equation is, $\pi_{obs} = i.cRT$

$$\text{Hence} \quad i = 1+(n-1)\alpha$$

$$\text{or} \quad \alpha = \frac{i-1}{n-1} \quad \dots \text{ (XI.29)}$$

As ' i ' is experimentally determined from freezing pt. measurement or measurement of other colligative properties, α is known. The degree of dissociation determined in this way is found to be practically the same as obtained from conductance measurements. Such identity confirms the explanation given above.

Problem 1. What would be the concentration in gms per litre of a solution of a non-electrolyte (mol. wt. 180) which would be isotonic with decinormal solution of sodium chloride, whose apparent dissociation is 85%?

$$\text{The osmotic pressure of NaCl solution,} \quad \pi = \frac{1+\alpha}{10} RT = \frac{1.85}{10} RT.$$

The osmotic pressure of the unknown solution, $\pi = \frac{w}{180} RT$ where w gms of the solute is present per litre.

$$\therefore \quad \frac{w}{180} = \frac{1.85}{10}, \text{ whence } w = 33.3 \text{ gms/litre.}$$

Problem 2. A solution containing 4.13 gms of lithium chloride per litre freezes at -0.343°C . Calculate van't Hoff's factor and the degree of dissociation.

$$\text{Mol-wt. of LiCl} = 7+35.5 = 42.5$$

$$\text{Calculated depression} = 1.86 \times \frac{4.13}{42.5}$$

$$\therefore \quad i = \frac{\Delta T_{obs}}{\Delta T_{theo}} = \frac{0.343 \times 42.5}{1.86 \times 4.13} = 1.898$$

$$\text{and degree of dissociation} \quad \alpha = \frac{i-1}{n-1} = i-1 = 0.898 \text{ i.e., } 89.8\%.$$

Reference for Further Reading

1. Text book of physical chemistry. Chapter IX—Glasstone.
2. Thermodynamics of solutions : Chem. Rev. 44.1, (1949).
3. Solubility of non-electrolytes (1950)—Hildebrand and Scott.

Problems

1. Deduce relationships between vapour-pressure lowering and the freezing pt. depression and the boiling point elevation of a solvent by a non-electrolyte solute.
2. What is the vapour pressure at 100°C of a solution containing 2 gms sucrose and 16 gms water. (Ans. 755 mm)
3. The boiling pt. of benzene is 80°C and it is raised to 82.3°C when 13.75 gms of diphenyl is added to 100 gms benzene. Find out the molal elevation constant and latent heat of vaporisation of benzene. (Ans. $L = 7500$ cal/mole)
4. 0.142 gm naphthalene in 20.25 gm of benzene lowered the freezing pt. by 0.284°C . Calculate the mol. wt. of naphthalene ($K_f = 5.12$). (Ans. 126)
5. A mixture of 1 gm naphthalene ($M = 128$) and 10 gm camphor freezes at 147°C , whereas pure camphor freezes at 177.5°C . What is the cryoscopic constant of camphor?

The melting point of a mixture of 1 gm acetanilide and 10 gms camphor is 148.5°C . What is the mol. wt. of acetanilide? Mol. wt. of camphor, 152. (Ans (a) 39.04°C (b) 134.6)

6. 100 gms of benzene contained 10 gms of a non-volatile solute (A). The loss in wt. of the solution in bubbling a slow stream of air through it was 1.205 gms. The same volume of air when passed through pure benzene the loss was 1.273 gms. What is the mol. wt. of (A)? (Ans. 130)

7. A solution of 0.174 gms of K_2SO_4 in 100 gms of water freezes at -0.05°C . Calculate degree of dissociation and apparent mol. wt.

8. What is the osmotic pressure of human blood as it is isotonic with 0.9 per cent NaCl solution at 27°C ? (Ans. 7.6 atmospheres)

9. The f. pt. of blood serum is -0.28°C , calculate its osmotic pressure in cms of Hg at 27°C ($K_f = 1.86$). (Ans. 284 cm)

10. The vapour pressure of an aqueous solution of cane sugar (mol. wt. 342) is 756 mm at 100°C how many gms of sugar are present in 1000 gms of water.

Calculate the freezing point of the solution also.

(Ans. 100.4 gms)

11. A solution of 3.6 gms of A in 150 c.c. water gave an osmotic pressure of 4.48 atmos. at 17°C . What is the b. pt. of the solution? ($K_b = 0.52$) (Ans. 100.098°C)

12. The osmotic pressure of a 3% aqueous solution of 'A' at 25°C is 3.632 atmospheres. What is the pressure of the solution at 25°C ? The vap. pressure of water at 25°C is 23.7 mm.

(Ans. 23.64 mm)

13. The f. pt. of a solution of 1 gm of a monobasic acid in 100 gm water was found to be -0.168°C and 0.2 gms acid was neutralised by 15.1 c.c. of 0.1 N NaOH. Show that the acid solution was 20.2% dissociated. ($K_f = 18.5$).

14. At 10°C , the osmotic pressure of a urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C when the osmotic pressure is found to be 105.3 mm. Determine the extent of dilution. (Ans. 5 times)

15. A solution of 1.73 gms of A in 100 c.c. water is found to be isotonic with a 3.42% solution of sucrose. Calculate molecular wt. of A. (Ans 173)

16. Calculate the mol. wt. of a substance 10 gm of which in 1000 c.c. of solution at 25°C exerts an osmotic pressure of 3 mm of Hg. (Ans. $M = 61990$)

17. The molality of dissolved gases in water at 0°C and 1 atm. is 1.29×10^{-3} . The decrease in volume during melting of ice is 0.0907 c.c./gm. The latent heat of fusion is 1436.3 cal/mol. The vapour pressure at triple point is 4.58 mm. Calculate the triple point temperature.

$$\Delta T = K_{f,m} = 1.862 \times 1.29 \times 10^{-3} = 0.0024^{\circ}\text{C}$$

Hence, when dissolved gases are removed, the f. pt. of water shall be $+ 0.0024^{\circ}\text{C}$.

$$\text{Again } L_f = 1436.3 \text{ cal} = \frac{1436.3}{18} \times \frac{82.05}{1.98} \approx 3290 \text{ c.c.-atm./gm.}$$

From Clapeyron eqn.,

$$\Delta T = \frac{T \cdot \Delta v}{l_f} \cdot \Delta p = \frac{273 \times (-0.0907)}{3290} \times \frac{(4.58 - 760)}{760} \approx + 0.0075^{\circ}\text{C}$$

$$\therefore \text{The triple-point temp.} = 0.0024 + 0.0075 = 0.0099^{\circ}\text{C}$$

ELECTROCHEMISTRY : CONDUCTANCE OF SOLUTIONS

XII.1. Electrolytes. Substances like mica, wax, glass, ebonite etc. strongly resist the flow of electricity and practically do not allow any current to flow through them. These are called *non-conductors*. But there are other substances such as copper, silver, mercury, water, solutions of salts, acids etc. through which electric current can easily pass ; these are called *conductors*. The conductors are broadly classified into two categories : (i) *electronic conductors* or metallic conductors and (ii) *electrolytic conductors* or electrolytes.

Electronic conductors in which are included the metals, alloys, graphite etc. are those where the electricity is carried exclusively by the transport of electrons. The electrons flow from a higher negative potential to a lower one ; there is no transport of matter during the passage of electricity.

In electrolytes, the flow of current is accompanied with actual transfer or migration of matter. It will be seen that such transfer of matter leads to the decomposition of matter at the points where electricity enters or leaves the electrolyte and in the process helps in the transfer of electrons. The electrolytes may be pure substances in fused states such as fused salts, bases, acids etc. or, more commonly, the electrolytes are solutions of salts, acids, bases usually in water and occasionally in other suitable solvents. The conducting capacity of different electrolyte is different.

The flow of electricity in both metallic and electrolytic conductors is governed by Ohm's law. In metallic conductors there is no chemical change whereas in electrolytic conductors there occurs chemical change or decomposition when the current is passed. There is another difference. With increase in temperature, the conductivity of electronic conductors decreases but that of the electrolytic conductors increases.

The decomposition of the electrolyte due to the passage of electricity is called *electrolysis*. The current usually enters or leaves the electrolyte through some rods or strips of metals or graphite etc ; these are called *electrodes*. The one through which the current enters is called the *anode* or positive electrode and the one through which the current leaves is the *cathode* or negative electrode. Electrolysis takes place only on the electrodes and not throughout the bulk of the electrolyte. Long before anything was known about the mechanism of the transport of electricity through the electrolyte, Faraday found out that there is a quantitative relation between the amount of electricity flowing through an electrolyte and the amount of chemical change occurring at the electrodes. These relations are universally applicable and are known as *Faraday's Laws*.

XII.2. Faraday's Laws of Electrolysis. The two laws discovered by Faraday are stated as follows :

(i) The amount of chemical change which occurs at any electrode is strictly proportional to the quantity of electricity passed through the electrolyte.

(ii) If the same quantity of electricity is passed through different electrolytes, the different amounts of chemical changes produced are all *chemically equivalent*.

Suppose W gms of a substance is deposited at an electrode when Q coulombs of electricity are passed, then from the first law

$$W \propto Q \text{ i.e., } W = zQ = zCt \quad \dots (XII.1)$$

when z is a constant called the *electrochemical equivalent*. It is the quantity of substance produced when 1 coulomb of electricity is passed, i.e., unit current (1 amp) passed for 1 second. C is the current in amperes and t is the time in second. Every substance has thus a definite electro-chemical equivalent (z). Thus,

by passing 1 coulomb of electricity 0.001118 gms of silver may be deposited at the electrode.

To illustrate the second law, let us take two solutions, say of NaCl and AgNO₃, in series in a circuit so that the same quantity of electricity is passed through both of them. In the first cell, chlorine will be liberated at the anode and NaOH will be obtained at the cathode with liberation of hydrogen. In the second cell, nitric acid will be formed and oxygen liberated at the anode while silver will be deposited at the cathode. If the current is passed long enough as to liberate 35.5 gms chlorine at the anode of the first cell, then it will be found that 40.0 gms of NaOH, 1.008 gms of H₂, 63 gms of HNO₃, 8.00 gms of O₂, and 107.88 gms of Ag have been produced at the other electrodes. That is, chemically equivalent amounts of different products are obtained.

The quantity of electricity required to liberate 1.008 gms of hydrogen or deposit 107.88 gms of Ag (*i.e.*, one equivalent of a substance) has been found to be 96493 coulombs. This quantity has been given the name *faraday*.

$$1 \text{ faraday} = 96493 \text{ coulombs} \approx 96500 \text{ coulombs}$$

If E_1 and E_2 be the chemical equivalents of two substances, whose electrochemical equivalents are z_1 and z_2 , then

$$E_1 = z_1 \times 96500 ; \quad E_2 = z_2 \times 96500$$

$$\text{or} \quad \frac{E_1}{E_2} = \frac{z_1}{z_2} \quad \dots \text{ (XII.2)}$$

i.e., the electrochemical-equivalents are proportional to the chemical equivalents of the substances.

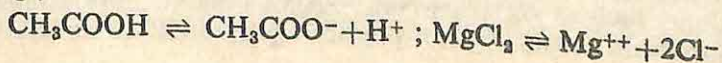
The accuracy of Faraday's laws is so high that an estimate of the amount of the chemical change in an electrolyte is used now for measuring the amount of electricity flowing. An electrolytic cell inserted in a circuit for this purpose is called a *coulometer*. The silver coulometer is extensively used. A Pt-basin, carefully dried and weighed, is used as the cathode in which a solution of (approximately 15%) AgNO₃ is taken. In the solution is suspended from above a thin anode of pure silver foil. The current is passed for about half an hour. Silver is deposited in the basin. The current is switched off. The basin is washed several times with pure distilled water, dried and weighed again to obtain the weight (W) of Ag deposited. Since z for silver is 0.001118, the quantity of electricity transferred $Q = W/z$ is known. Copper-coulometer, gas-coulometers or iodine coulometers are also used for this purpose.

XII.3. Electrolytic Conduction : Arrhenius Theory of Electrolytic Dissociation.

Attempts to explain the behaviour of electrolytes in conducting electricity had been made by various investigators like Faraday, Berzelius, Grotthus, Clausius and others. But a clear picture of the mechanism of the flow of electricity through electrolytes and the consequent electrolysis was presented first by Arrhenius in 1887. The basic postulates of his theory are believed to be correct even today. Arrhenius observed that the conductivity of solutions of electrolytes increased with dilution and reached a limiting value at very high dilutions. This led him to conclude that the number of those species responsible for carrying the current increases with dilution. From the results of his experiments, Arrhenius proposed his theory of electrolytic dissociation which may be stated as follows.

(i) A portion of the electrolyte in solution is dissociated into positively charged and negatively charged particles. These charged particles are positively charged particles are *cations* and the negatively charged particles are *anions*. These ions are really responsible for carrying the electricity through the solution. Under a potential gradient, cations move towards the negative electrode or cathode and the anions move towards the positive electrode or anode. The extent of dissociation is different for different electrolytes and would also depend on the solvent and the temperature.

(ii) There is an equilibrium between the ions and the undissociated electrolyte molecules, *e.g.*,



The properties of the charged particle are entirely different from those of the neutral atom. We now know that the ions are formed by the removal from, or addition of electrons to, the neutral atoms.

(iii) The number of the positively charged cations and negatively charged anions may be different, but the total +ve charge carried by the cations is equal to the net -ve charge carried by the anions. So, the electrolyte solution at any instant remains neutral.

(iv) When the cations reach the cathode, they are neutralised and neutral molecules or groups are formed there. Similarly, when the anions reach the anode they give up their negative charge at the electrode and become neutral. This shows that electrolysis occurs only at the electrodes.

It is now known that cations receive electrons from the cathode and the anions give up their electrons to the anode. That is, electrons pass from cathode to the solution and from solution to the anode. This means that though current flows from anode to cathode, the electrons are really flowing unidirectionally from cathode to anode, *i.e.*, opposite to the flow of electricity. The cations and anions travelling oppositely really help the electrons to flow unidirectionally.

The conductivity of a given amount of electrolyte, as already stated, increases with increasing dilution. At very high or infinite dilution, the conductivity reaches a maximum limiting value. Since ions are assumed to conduct the electricity, their numbers, *i.e.*, the extent or degree of dissociation must increase with dilution. Hence if λ_v and λ_0 denote the conductivities of a given amount of electrolyte at dilution v and at infinite dilution, then degree of dissociation (α) of the electrolyte at dilution v is given by,

$$\alpha = \frac{\lambda_v}{\lambda_0} \quad \dots \text{ (XII.3)}$$

When Arrhenius was working on the conductivity of electrolytes, van't Hoff's findings about the abnormal behaviour of solutions of electrolyte in respect of their colligative properties such as osmotic pressure, boiling point elevation, etc. were just published. The solutions of non-electrolyte obey the van't Hoff relation $\pi = CRT$. But when electrolyte solutions are taken, the observed osmotic pressure (π_{obs}) is found to be much higher than that calculated from the relation mentioned above (sec. XI.16). van't Hoff did not give any explanation for the same, and expressed the deviation by the factor i , such that

$$i = \frac{\pi_{obs}}{\pi_{calc}}, \text{ or } \pi_{obs} = i \cdot \pi_{calc} = iCRT$$

Identical deviation was found when other colligative properties were studied such as freezing point depression, or boiling point elevation.

It was logically argued that when RT was constant, higher osmotic pressure must be due to an increase in concentration C , *i.e.*, the number of particles present in solution of the electrolytes.

Arrhenius suggested that this was due to the dissociation of a fraction of the electrolyte molecules giving a higher total of individual particles in solution, the ions having separate entities. Hence

$$\pi_{obs} = [1 + (n-1)\alpha]CRT = iCRT$$

where α is the degree of dissociation, and n is the number of ions produced from each molecule.

$$\therefore i = 1 + (n-1)\alpha, \text{ or } \alpha = \frac{i-1}{n-1} \quad \dots \text{ (XII.4)}$$

The degree of dissociation obtained from conductivity results (XII.3) was found in good agreement with the values obtained independently from colligative properties (XII.4). This demonstrates the correctness of the theory of electrolytic dissociation.

There are other evidences which point to the dissociation theory. The precipitation reactions, such as $\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{NaNO}_3$, are explained on the basis of dissociation theory. Many physical properties of colligative nature,

such as colour, refractive index etc. support the ionisation theory. All permanganates in solution are pink, chromates yellow etc. and the intensity of colour is proportional to concentration indirectly prove ionisation. X-ray studies of salt crystals have now also confirmed the existence of ions even in their crystal lattice. Aqueous solutions of iodides when vigorously centrifuged had one end positive and the other end negative (Tolman) ; this is possible only if the iodides are dissociated into ions having different mobilities.

The Charges Carried by Ions : Avogadro Number. We have seen that 1 gm-equiv. of a substance is deposited or dissolved at an electrode when 1 faraday of electricity is passed. Thus for the discharge of 1 gm of hydrogen or 35.5 gms of chlorine, one faraday is required. In the electrolysis at the electrodes, hydrogen ions take up electrons and chloride ions give up electrons. Hydrogen ions are considered to carry unit positive charge and chloride ions unit negative charge. Now 1 gm of hydrogen (i.e., 1 gm-atom) contains Avogadro number (N_0) of hydrogen ions. So also 35.5 gms or 1 gm-atom of chlorine.

If ϵ represents the unit charge, then the total charge in a gm-atom of hydrogen or chloride ions would be $N_0\epsilon$.

$$\text{Hence} \quad N_0\epsilon = \mathcal{F} \text{ (one faraday)}$$

$$\text{or the Avogadro number} \quad N_0 = \mathcal{F}/\epsilon \quad \dots \text{ (XII.5)}$$

Both $\mathcal{F}$ and ϵ are universal constants determined independently. Their accurate values are $\mathcal{F} = 96493$ coulombs, and $\epsilon = 1.602 \times 10^{-19}$ coulombs. The Avogadro Number N_0 is then 6.02×10^{23} . This indeed is an accurate method for the estimation of Avogadro number.

On the other hand, when 1 gm of hydrogen is deposited at an electrode, 32.5 gms of zinc would also be deposited by the same quantity of electricity. That is 32.5 gms is the gm-equivalent of zinc, whose mol. wt. is known as 65. It is thus seen that 1 gm molecule of zinc or N_0 number of zinc ions would carry two faradays of electric charge. In other words, each zinc ion will carry double the charge carried by a hydrogen ion. A zinc ion will carry two units of positive charge. In general, an ion carries the number of charges equal to its valency.

XII.4. Strong and Weak Electrolytes. The extent or degree of dissociation of different electrolytes in solution is different. Substances which are largely dissociated and render the solution in water highly conducting are called *strong electrolytes*. All salts, mineral acids like HCl, H_2SO_4 , HNO_3 , etc. and bases such as NaOH, KOH etc. dissociate practically completely in solution in water and are strong electrolytes. Such acids or bases are hence named strong acids and strong bases.

On the other hand, there are many substances which dissociate only to a small extent in aqueous solution. The solutions of such substances have low conducting power. Such substances are *weak electrolytes*. The carboxylic acids, phenols, some inorganic acids like HCN, HBO_3 , H_4SiO_4 , etc. and bases like ammonia, amines, etc. are examples of weak electrolytes. There are a few salts, such as mercuric chloride which have also a small degree of dissociation.

This division into strong and weak electrolytes is a qualitative one. There are some electrolytes, such as trichloroacetic acid solution, which exhibit an intermediate behaviour. In deciding the nature of an electrolyte—strong or weak—the aqueous solutions are considered. It must be remembered that the nature of the solvent plays an important part in the degree of dissociation of the dissolved substance. Generally, the higher the dielectric constant of the solvent, the greater is the chance of dissociation. Besides the dielectric constant of the solvent there are also other factors, such as hydrogen-bonding with solvent molecules, which also influence the degree of dissociation considerably.

MIGRATION OF IONS

XII.5. Transference Numbers. Under a potential gradient current is transported by the migration of ions, the positive ions moving towards the cathode, the negative ions towards the anode. The total charge released at the cathode and at the anode are of course equal but the fraction of the total current conveyed by the

cations and the anions through the solution are not necessarily equal. For example, in a dilute solution of nitric acid, only 16% of the current is conveyed by NO_3^- ions, the rest by the H^+ ions. In a dilute copper sulphate solution, Cu^{++} ions transport 38% of the current and SO_4^{--} ions transport 62%. The transport of current by ions in a solution depends upon not only the charge and number of the ions but also on the speed of the ions. It is obvious that having same charge the ions with greater speed will pass a section of the solution in greater numbers than those with a lower speed. Hence the former would transport a larger amount

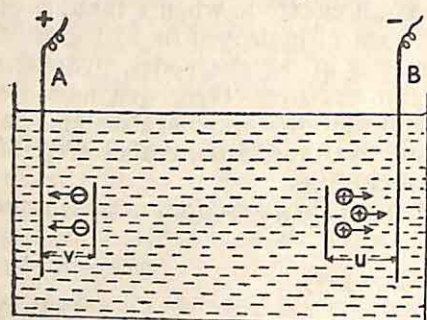


FIG. XII.1

of current. A relation between the speed of an ion and the fraction of current conveyed by it may be obtained in the following way.

Let us take an electrolyte between two electrodes *A* and *B* as in Fig. XII.1. Let the number of cations per cc. of the solution be n_+ each carrying a charge z_+ . Suppose the current passing through the solution be I under a potential difference of E volts. Further suppose that u and v are the velocities of the cation and anion respectively under this voltage. Consider now only unit cross-section of the two

electrodes, when the current passes just for a second. It is evident that all the anions which are within a distance v from the anode would reach *A* and during this time all the cations within a distance u from the cathode would reach *B*. Remembering unit cross-section, the number of cations and anions to be discharged on *B* and on *A* are n_+u and n_-v respectively. If the quantity of electricity associated with unit charge be represented by e , then

the current carried by cations, $I_+ = (n_+u)z_+e$

and the current carried by anions, $I_- = (n_-v)z_-e$

The total current carried by the cations and anions together,

$$I = I_+ + I_- = n_+z_+e.u + n_-z_-e.v \\ = n_+z_+e.u + n_+z_+e.v, \quad \dots \text{(XII.6)}$$

the solution being electrically neutral, we have $n_+z_+ = n_-z_-$.

It may be remembered that though physically the ions migrate in opposite directions, these help the passage of current in the same direction.

The fraction of the current carried by cations and anions, represented by t_+ and t_- , are called *transport* or *transference* numbers. These would be,

$$(a) \quad t_+ = \frac{I_+}{I} = \frac{n_+z_+eu}{n_+z_+eu + n_+z_+ev}$$

or transference number of cation, $t_+ = \frac{u}{u+v} \quad \dots \text{(XII.7)}$

$$\text{and (b)} \quad t_- = \frac{I_-}{I} = \frac{n_-z_-ev}{n_+z_+eu + n_+z_+ev}$$

or transference number of anion, $t_- = \frac{v}{u+v} \quad \dots \text{(XII.8)}$

$$\text{Further,} \quad t_+ + t_- = 1; \text{ and } \frac{t_+}{t_-} = \frac{u}{v} \quad \dots \text{(XII.9)}$$

XII.6. Hittorf's Rule. Because of the different velocities of anions and cations, the concentration changes in the vicinity of the anodes and cathodes are also different.

It must however be remembered that the solution as a whole is always neutral and that amounts of cations and anions liberated at the respective electrodes are in equivalent quantities.

The changes in concentration of the electrolyte near the cathode and the anode can be easily visualised in the following way. Consider an electrolyte between two electrodes as in Fig. XII.2, in which positive and negative ions are represented by + and - signs.

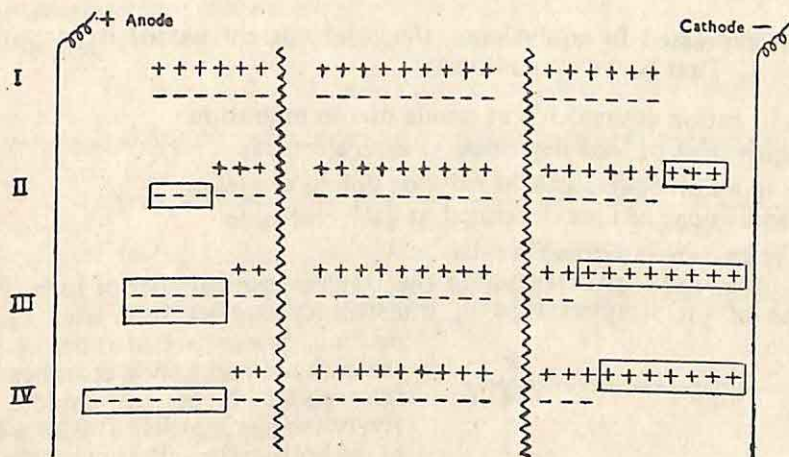


FIG. XII.2 Migration of ions

Before the passage of current, the condition of the ions are as shown in I of the figure. An equal distribution of +ve and -ve ions is present everywhere. Let us imagine the cell divided into three chambers by two partitions shown by serrated lines, so that we have a cathode chamber, a central chamber and an anode chamber. Let us also take equal number of cations and anions in each of cathode and anode chambers, each having say, six +ve and six -ve ions.

Now suppose on application of a field, only the cations move but the anions remain stationary. Suppose the current flows for such time that every cation moves only three steps forward. Three cations cross each partition, so that there are three excess cations in cathode chamber and three excess anions in the anode chamber. This is represented in II. Since each compartment should be electrically neutral, so three cations are discharged on the cathode and three anions on the anode. It is thus seen that though the anions did not move, yet these were discharged in amounts equivalent to that of the cations. Moreover, the motion of the cations caused a fall in the concentration of electrolyte in the anode chamber. The anions did not move and hence the concentration in the cathode chamber remained unaltered.

In the next case III, let us consider that both anions and cations are moving at equal rate, say each ion moves four steps in its respective direction in a given time. At the end of this time interval, there shall be eight excess anions in the anode chamber and eight excess cations in the cathode chamber, all of which would be discharged as the solution in both chambers had to be electrically neutral. We now find that when the speeds of both ions are the same, the fall in concentration in both the anode and the cathode chambers is also equal. The amount of ions discharged at each electrode is proportional to the sum of the speeds of the two ions.

Now let us suppose cations and anions are moving with unequal speeds. Suppose each cation moves four steps and each anion three steps in their respective directions in a given interval of time. The condition is represented in IV. The excess anions would be seven in the anode chamber and the excess cations also seven in the cathode chamber. These ions would be discharged at the corresponding electrodes. The amounts discharged at each electrode are not only equal but also proportional to the sum of the speeds of the two opposite ions. Further

the fall in concentration in the anode chamber is proportional to the speed of cations. The fall in concentration in the cathode chamber is proportional to the speed of anions. It is also seen that the concentration in the central chamber remains unaffected.

We are thus led to the conclusion that due to passage of a current,

$$\frac{\text{Loss in cation concentration at anode due to migration}}{\text{Loss in anion concentration at cathode due to migration}} = \frac{u}{v} = \frac{t_+}{t_-}$$

When expressed in equivalents, the total current passed is proportional to $t_+ + t_- = 1$. That is, we may also say,

$$\frac{\text{Loss in cation equivalents at anode due to migration}}{\text{equivalent of ions deposited at each electrode}} = t_+ \quad \dots \text{(XII.9)}$$

$$\text{and } \frac{\text{Loss in anion equivalents at cathode due to migration}}{\text{equivalent of ions deposited at each electrode}} = t_- \quad \dots \text{(XII.10)}$$

This is known as *Hittorf's rule*.

It is often used in determining the transference number of ions. Fig. XII.3 shows one of the simplest type of transference number tube used in Hittorf's method. It consists of tubes A and B as the cathode and anode chambers with the intervening C as the middle portion. Every section is provided with a stop cock at the bottom for withdrawing the solution. Electrodes are inserted through corks at the top. In the circuit in series are connected a milliammeter (M), a silver coulometer (X), and a resistance (R). The transport number tube (ACB) is filled with the electrolyte under examination. A current of 20 milliamperes or so is then passed for three hours so that concentration changes are appreciable. In the silver coulometer is taken a solution of (approximately) $N/10$ AgNO_3 . From the silver deposited on the Pt-basin of the coulometer, the equivalent of current passed or the equivalents of ions deposited in the other electrodes in the circuit are accurately known (Faraday's laws).

Since it is required to measure the concentration change due to migration of ions, adequate precautions are taken to prevent diffusion, convection or mechanical disturbance of the solution. When the current is stopped, the solution is drained out from one or both the chambers, weighed and then analysed. The loss or gain in concentration of the electrolyte in the chambers is known and is expressed in terms of equivalents for a definite weight of the solvent. From these the transference number can be easily computed. Let us illustrate this with a solution of copper sulphate.

Suppose initially the Hittorf tube is filled with a 0.1 molal solution of copper sulphate and electrolysed between copper electrodes.

After electrolysis, let the amount of solution taken out from the cathode chamber be w_1 gms, which, on analysis (iodometrically), was found to contain w_2 gms of copper.

Further suppose, the increase in weight of the cathode in the coulometer due to deposit of silver be w_3 gms.

(the equivalent weight of Ag = 107.88, mol. wt. of copper sulphate = 159.6)

It is evident that the total quantity of electricity passed is given by w_3 gms of silver i.e.,

$$\frac{w_3}{107.88} \text{ equivalents} = Z \text{ faradays (say).}$$

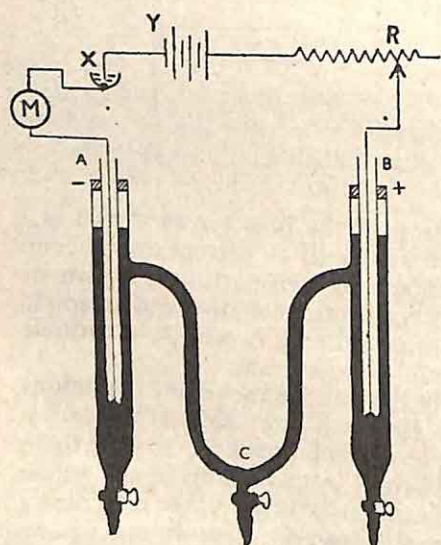


FIG. XII.3 Transference number detn. by Hittorf's method

In the cathode chamber then Z equivalents of copper must have been deposited. But the loss in the concentration in this chamber would be less than Z , for other Cu^{++} ions have meantime migrated into this chamber.

$$\begin{aligned}\text{Now } w_2 \text{ gms of copper} &\equiv w_2 \times \frac{\text{CuSO}_4}{\text{Cu}} \equiv w_2 \times \frac{159.6}{63.5} \\ &\equiv w_2 \times 2.512 \text{ gms of copper sulphate} \\ &\equiv y \text{ gms (say)}\end{aligned}$$

That is, the cathode solution analysed contained $(w_1 - y)$ gms of water.

In the initial state $(w_1 - y)$ gms water was associated with

$$(w_1 - y) \times \frac{0.1 \times 159.6}{1000} \text{ gms of copper sulphate} = x \text{ gms (say).}$$

That is, the actual loss in the amount of copper sulphate in the cathode solution

$$= (x - y) \text{ gms of } \text{CuSO}_4 = \frac{(x - y) \times 2}{159.6} \text{ equivalents}$$

We can now see that Cu^{++} migrating into the cathode solution $= Z - \frac{2(x - y)}{159.6}$ equivalents

where Z is the total deposit of an ion in equivalents. The transference number of the Cu^{++} ion in the solution is then

$$t_+ = \frac{Z - 2(x - y)/159.6}{Z}$$

and that of the SO_4^{--} ion

$$t_- = 1 - t_+ = \frac{2(x - y)/159.6}{Z}$$

XII.7. Moving Boundary Method. In this method, the transference number is determined by directly following the speeds of ions under an applied potential. A device is made in which the boundary between two ionic solutions is clearly distinguishable. By passing a suitable current the transfer of the boundary enables one to calculate the transference number. A diagrammatic sketch of the apparatus used is given in Fig. XII.4.

The vertical tube PQ is the electrolytic cell. This has a narrow but uniform bore, which is carefully measured. Suppose the transference numbers of the ions of MA (say HCl) are to be determined. The solution of MA is placed in the tube between two indicator solutions $\text{M}'\text{A}$ and MA' , one having common anion and another having common cation with the given electrolyte, say CdCl_2 and HAc , as shown. The three solutions are taken in increasing density downwards so that mixing is avoided. The indicators ($\text{M}'\text{A}$ and MA') are so chosen that the speed of M' is less than that of M , and the speed of A' is less than that of A . Here, Cd^{++} has a lower speed than that of H^+ , and the speed of Ac^- is less than that of Cl^- . The lower part of the tube is filled with CdCl_2 solution with a Cd -anode in it. A Pt -cathode is inserted at the top in the HAc solution. The circuit also contains a coulometer (C), milliammeter (M) and a resistance (R). The junction of the HCl and CdCl_2 solution is quite sharp and distinguishable. The current is next switched on. The H^+ ions move upwards, much faster than the Cd^{++} ions following. The result is that the boundary slowly moves upwards from xx' to yy' during the period of electrolysis. The displacement (l) of the boundary is accurately measured, say by a cathetometer.

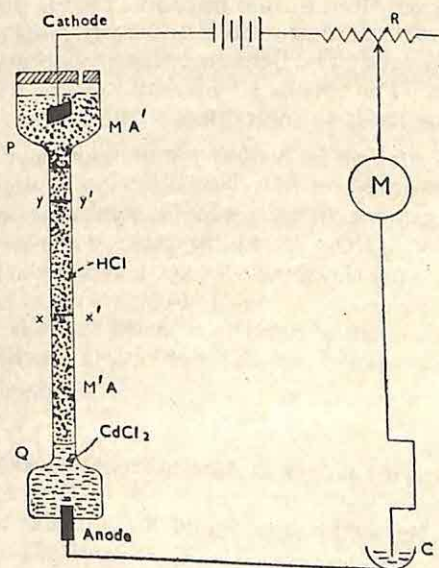


FIG. XII.4 Transference number by moving boundary method

If the cross section of the tube be ' a ', then the volume swept out by the boundary in moving from xx' to yy' is $(l \times a)$ c.c. If c be the concentration of the HCl

solution, the amount of acid moved upwards during the experiment is $la.c/1000$ gm equivalents.

If, further, Q faradays of electricity have been passed during electrolysis, known from the coulometer, then the fraction of the current transported by H^+ ions is t_+Q faraday. Hence, t_+Q gm-equivalent H^+ ions have migrated.

$$\therefore t_+Q = \frac{lac}{1000}$$

$$\text{or } t_+ = \frac{lac}{1000 \times Q} \quad \dots (XII.11)$$

Quite a number of precautions are to be taken in carrying out the experiment for which a standard text on electrochemistry may be consulted.

There is also a method for determination of transference number from electromotive force measurement of some suitable cells, which will be discussed in Chapter XIII. In the tables below are given the transference numbers of ions for some electrolytes in aqueous solutions.

TABLE : TRANSFERENCE NUMBERS OF CATIONS AT 25°C IN 0.1N SOLUTION

Electrolyte	t_+	Electrolyte	t_+
HCl	0.834	NaOH	0.183
LiCl	0.317	KOH	0.265
NaCl	0.385	CuSO ₄	0.373
KCl	0.490	CdSO ₄	0.364
KNO ₃	0.510	KI	0.492
AgNO ₃	0.468	KBr	0.492

An interesting point revealed from the results tabulated above may be mentioned here. From a consideration of the atomic structure and also from experimental observation with X-ray diffraction, it is known that lithium ion has a smaller volume than that of sodium and potassium. Their volumes are in the order lithium, sodium, potassium. These ions are therefore expected to have velocities decreasing in the same order lithium, sodium, potassium. The transference number results however indicate that lithium ion moves slower than sodium ion and the latter slower than potassium ion. This is due to the fact that lithium ion has a stronger electric field around it and so attracts a number of water dipoles and is thus heavily hydrated. The field surrounding potassium ion is feeble and degree of hydration is less. The result is hydrated lithium ion is larger than the hydrated potassium ion. This leads to their speeds being in the order potassium, sodium, lithium.

Problem 1. A silver nitrate solution containing 0.00739 gm of AgNO₃ per gm of water is electrolysed between silver electrodes. During the experiment 0.078 gms of Ag was deposited on the cathode. At the end of the experiment anode solution contained 23.14 gms of H₂O and 0.236 gm of AgNO₃. What is the transport number of Ag⁺?

After electrolysis, the anode solution has

(a) 23.14 gms water

(b) 0.236 gms AgNO₃

The amount of AgNO₃ associated with this water initially was = $23.14 \times 0.00739 = 0.171$ gms.
The amount of AgNO₃ formed due to dissolution of Ag from the anode during electrolysis

$$= \frac{0.078 \times 170.88}{107.88} = 0.122 \text{ gm}$$

Hence, the amount of AgNO₃ which migrated away from the anode chamber

$$= 0.171 + 0.122 - 0.236 = 0.057 \text{ gms.}$$

The total current passed

$$= 0.078 \text{ equivalents of Ag}$$

$$= 0.122 \text{ equivalents of AgNO}_3$$

Hence

$$t_{Ag^+} = \frac{0.057}{0.122} = 0.46$$

Problem 2. In an experiment for the determination of transport numbers of ions in 1.00N KCl by moving boundary method, the indicator electrolyte following was 0.75 N BaCl₂. The boundary swept a volume of 0.1200 c.c. in 1670 sec when a current of 0.014 amp was passed. What is the transport number of Cl⁻ ions?

The quantity of electricity passed, $Q = \frac{0.014 \times 1670}{96500}$ faradays

The amount of KCl moved towards cathode $= \frac{0.1200 \times 1.00}{1000}$ equivalents.

Hence transport of electricity by K^+ ,

$$t_+ = \frac{0.1200 \times 96500}{1000 \times 0.014 \times 1670} = 0.495$$

$\therefore$ Transport number of Cl^- ions, $t_- = 1 - t_+ = 0.505$.

CONDUCTANCE OF SOLUTIONS

XII.8. Electrolytic Conductance. As for metallic conductors, the resistance is measured with the help of Ohm's Law, which states

$$R = E/I$$

where E is the applied voltage and I is the current passing through the conductor. The resistance is a measure of the opposition to the flow of electricity through the given conductor. Ohm's law is also equally valid for electrolytic solutions. The resistance of electrolyte solutions being large it would be more convenient to give our attention to the *conductance* of solutions than to their *resistance*. Literally as also mathematically, the conductance is the inverse of resistance. The conductance is a measure of the ease or readiness with which the current is conveyed through the solution. The conductance (A) is the reciprocal of the resistance (R).

$$A = \frac{1}{R} \quad \dots (XII.12)$$

The resistance is expressed in units of ohm, the conductance has units of *reciprocal ohm* (or *mho*).

It is known that the resistance of a conductor depends upon its length (l) and cross-section (a), such that

$$R = \rho \cdot \frac{l}{a} \quad \dots (XII.13)$$

where ρ is the *specific resistance*. It is the resistance of unit length of a conductor of unit cross-section. The specific conductance (L) is the reciprocal of specific resistance.

$$L = \frac{1}{\rho} \quad \dots (XII.14)$$

The conductance of a given electrolyte solution between two electrodes of cross-section A sq. cms and l cms apart would be,

$$A = \frac{1}{R}$$

$$\text{or} \quad A = \frac{1}{\rho} \cdot \frac{a}{l} = L \cdot \frac{a}{l} \quad \dots (XII.15)$$

$$\text{or} \quad L = \frac{l}{a} \cdot A = \frac{l}{a} \cdot \frac{1}{R} \quad \dots (XII.16)$$

If $a = 1$, $l = 1$, the specific conductance $L = \lambda$. That is, the specific conductance is the conductance of the solution enclosed between two electrodes of 1 sq. cm area and 1 cm apart.

In dealing with electrolytic solutions, a quantity of greater importance is the *equivalent conductance* (λ) of the solution. It is defined as the conductance of a solution containing 1 gm-equivalent of the dissolved electrolyte such that the entire solution is placed between two electrodes 1 cm apart. As direct determination of this quantity with equation (XII.16) would need electrodes of enormous sizes, the equivalent conductance is always evaluated through measurement of specific conductance.

If the solution of electrolyte has a concentration of C equivalents per litre, the volume of the solution containing 1 gm-eqv. would be $1000/C$ c.c. If this volume be imagined to be placed between two electrodes 1 cm apart, the cross-section of the column of solution or electrodes would be $1000/C$ sq. cms. The equivalent conductance of the solution would be (eqn. XII.15),

$$\lambda = \frac{a}{l} L = \frac{1000}{C \times 1} \times L = \frac{1000L}{C} \quad \dots \text{(XII.17)}$$

L being the specific conductance.

This relation is universally employed to obtain the equivalent conductance (λ) through the determination of specific conductance (L).

XII.9. Determination of Conductance. For the determination of specific conductance, a wheatstone-bridge setup is used, as in Fig. XII.5. In one arm of the bridge, the solution is taken in a specially constructed bottle or *conductivity cell*. A few of the various types of conductivity cells used are shown in Fig. XII.6.

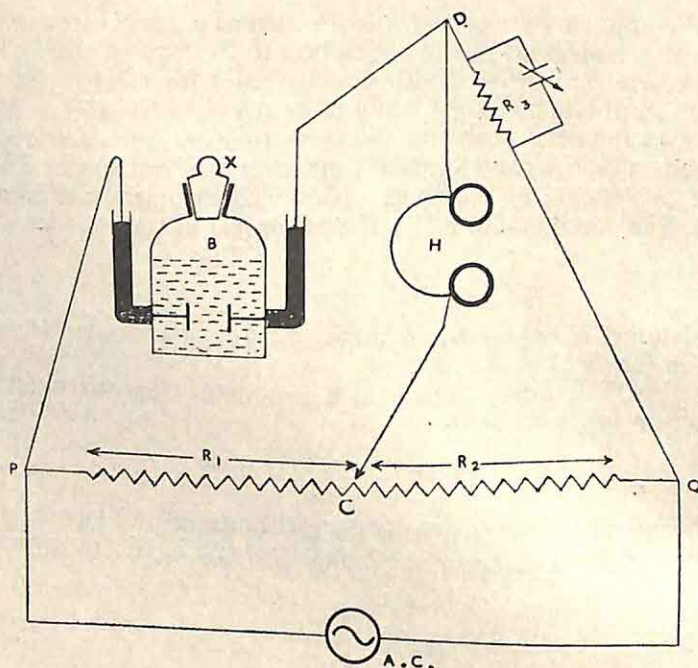


FIG. XII.5 Diagram for conductivity determination circuit

In general, the conductivity cells are stoppered glass bottles, inside which there are two similar Pt-electrodes fused to the walls of the vessels through Pt-wires. These wires are led into two arms of the bottle, so that the electrodes are connected to the electric circuit through mercury contacts. Inside, the electrodes are placed opposite to each other and are coated with Pt-black. The distance

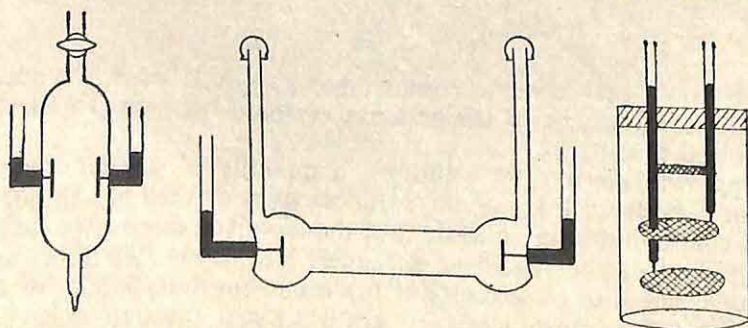


FIG. XII.6 Different types of conductivity cells

between the electrodes for any cell is thus fixed. For solutions of poor conductance, the electrodes are mounted very near to each other; for solutions with high conductance the electrodes may be widely spaced.

In the experimental arrangement, the solution is taken in the conductivity cell *B* and connected to one arm of the bridge, the other arm *DQ* carries a variable resistance R_3 . *PQ* is a uniform slide-wire on which moves a contact point 'C'. This contact point *C* is connected through an earphone to the point *D* junction of the other two arms *PD* and *QD* containing the cell and the variable resistance R_3 . An alternating current (say 1000 cycles) is used in the circuit. The current should be an alternating one as otherwise electrolysis would occur in the cell and concentration would change. The temperature is controlled by keeping the cell partially immersed in a thermostat. The current from the source enters at *P* and *Q* and divides into two parallel branches along *PCQ* and *PDQ*.

Using a definite resistance R_3 in the arm *DQ*, the contact point *C* is moved along the slide-wire until no sound is produced in the earphone, i.e., until no current passes along *DC*. Under this condition, potentials at *C* and at *D* are the same, hence

$$\frac{X}{R_3} = \frac{R_1}{R_2}, \text{ or } X = \frac{R_1}{R_2} \cdot R_3$$

where *X* is the resistance of the solution. R_1 and R_2 are the resistances of the two portions of the slide-wire, the ratio arms. In fact, the R_1/R_2 is the ratio of the lengths *CP/CQ*, when a wire of uniform cross-section is used. The resistance of the solution (*X*) taken in the cell is thus known.

Theoretically when balance point is reached by moving the contact point *C*, there should be no sound in the earphone. But due to capacitance arising from the cell, some little sound still occurs at the balance point. The point where the sound is minimum is taken as the balance point. By inserting a variable condenser parallel to the standard resistance R_3 , the capacitance effect of the conductivity cell can be annulled to a large extent and a much improved balancing is possible.

But to know the specific resistance, it would be necessary to determine the cross-section and the distance of the electrodes of the cell used. These determinations are not quite easy. In fact the ratio (*l/a*) of the cell, called *cell constant* is ascertained in another way.

Using conductivity cells of accurately known dimensions (*l* and *a*) Kohlrausch and his co-workers determined very precisely the specific conductance of standard solutions of pure KCl at different temperatures. Some of the values of specific conductances of KCl solutions are quoted below from standard tables.

TABLE : SPECIFIC CONDUCTANCES OF KCl SOLUTIONS

Conc. in eqv./litre	<i>L</i> in mhos		
	0°C	18°C	25°C
0.01	0.0007751	0.0012227	0.0014114
0.10	0.007154	0.011192	0.012886
1.00	0.06543	0.0982	0.11173

In order to ascertain the cell-constant (*l/a*) of the conductivity cell used in the laboratory, the resistance of KCl sol. of 0.1 or 0.01 molar strength is measured in this cell with the wheatstone bridge circuit as described above. Suppose the resistance of the KCl solution is found to be '*r*'. From equation (XII.16),

$$\text{the cell constant} \quad K = \frac{l}{a} = L_s r$$

where L_s is the specific conductance of KCl sol. known from the Table. The cell-constant for the particular cell is thus known.

For a given solution, the resistance (R) is measured in the usual way with the wheatstone-bridge. The specific conductance (L) of the solution (from equation XII.16), is then

$$L = \frac{l}{a} \cdot \frac{1}{R} = K/R$$

Since l/a and R are both known, the specific conductance of the given solution is also known.

The equivalent conductance of the given solution is then obtained with equation (XII.17),

$$\lambda = \frac{1000 \times L}{C}$$

It may be mentioned that in preparing the solutions, 'conductivity water' i.e., highly purified water obtained from repeated distillation in an all quartz apparatus has to be used.

Problem 3. At 18°C , the resistance of $0.1N$ KCl in a conductivity cell is 86.8 ohms and that of $0.05N$ NaCl is 203 ohms. What is the equivalent conductivity of $0.05N$ NaCl?

We know from the table that the specific conductance of $0.1N$ KCl at 18°C is 0.011192 mhos.

The cell constant, $K = \frac{l}{a} = L_{\text{KCl}} \times \text{resistance} = 0.011192 \times 86.8$

The specific conductance of the NaCl solution is

$$L_{\text{NaCl}} = \frac{l}{a} \times \frac{1}{R} = \frac{0.011192 \times 86.8}{203} \text{ ohm}^{-1} \text{ cm}^{-1}$$

The equivalent conductance of $0.05N$ NaCl is then,

$$\lambda = \frac{1000}{C} \times L_{\text{NaCl}} = \frac{1000}{0.05} \times \frac{0.011192 \times 86.8}{203} = 95.71 \text{ ohm}^{-1} \text{ cm}^2$$

The equivalent conductances of a few electrolytes are given in the table below.

TABLE : EQUIVALENT CONDUCTANCES (25°C)

Conc. (N)	HCl	NaOH	KCl	NaCl	AgNO ₃	CH ₃ COOH	NaAc
1.000	332.8	—	111.9	—	—	—	49.1
0.100	391.32	221.0	128.96	106.74	109.14	5.20	72.80
0.010	412.00	237.0	141.27	118.51	124.76	16.20	83.76
0.001	421.36	245.0	146.95	123.74	130.51	48.63	88.5
0.0005	422.74	246.0	147.81	124.50	131.36	135.0	89.2
∞ -dilution	426.16	248.1*	149.9	126.45	133.3	391*	91.0

*Calculated from ion conductances

XII.10. Equivalent Conductance and Concentration. Even a cursory glance of the table just given will show that the equivalent conductance varies appreciably with concentration. With increasing dilution, the equivalent conductance also increases. It is necessary to consider the effects of dilution on equivalent conductance separately for strong and for weak electrolytes.

Strong electrolytes. Solutions of salts like KCl, CaCl₂, Na₂SO₄, NaAc, etc. or acids such as HCl, H₂SO₄ etc. have very high equivalent conductance even at ordinary concentrations. With dilution their conductances increase to some extent and ultimately tend to reach a limiting value. The conductance when the solution is infinitely dilute is called the *equivalent conductance at infinite dilution*, denoted by λ_0 . It is indeed the value of equivalent conductance reached at very high dilution such that any further dilution would not change it.

It was Kohlrausch who suggested an empirical relation from experimental results between the concentration, c and the equivalent conductance λ_c , expressed as

$$\lambda_c = \lambda_0 - b\sqrt{c} \quad \dots \text{(XII.18)}$$

where b and λ_0 are constants for a given electrolytic solution. At very low

concentration, *i.e.*, at infinite dilution evidently $\lambda_c = \lambda_0$. The plot of λ_c vs $\sqrt{c}$ is almost linear for many electrolytes as shown in Fig. XII.7. Extrapolation of the linear portion at high dilutions to $\text{Lt. } c \rightarrow 0$ gives the value of λ_0 , the equivalent conductance at infinite dilution.

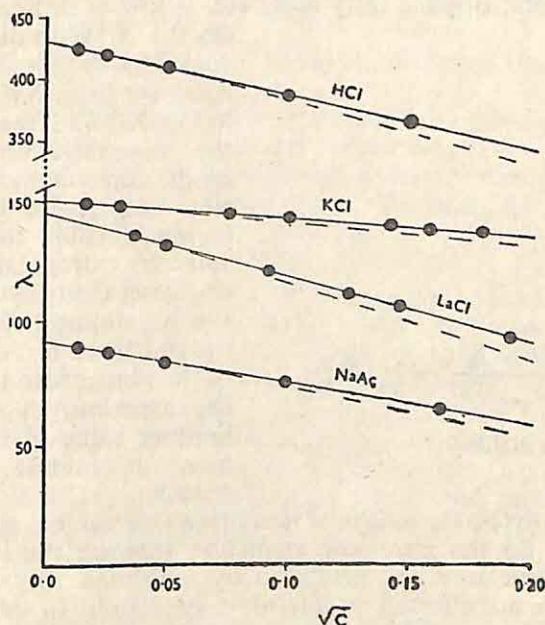


FIG. XII.7 Ekv. conductance of strong electrolytes vs $\sqrt{c}$ in aqueous medium

In fact, the classification of electrolytes into strong and weak ones may be based on their behaviour in respect of the variation of equivalent conductance with dilution. The change in equivalent conductance of strong electrolytes with dilution is relatively small and the limiting value is easily reached experimentally. We shall presently see that weak electrolytes behave differently and that with dilution their equivalent conductances vary enormously.

At present the accepted idea is that strong electrolytes (HCl, NaOH, NaAc, KCl) are completely ionised in solution even at ordinary concentrations. It has now been confirmed from X-ray studies of salt crystals that even in the solid state, the positive and negative ions exist in the lattice. The salts have ionic lattices and are strong electrolytes. Obviously when dissolved, all these ions are released from the lattice bonds and these are responsible for conducting the electricity. We are thus led to conclude that in all reasonable concentrations, the substances having ionic lattices, *i.e.*, strong electrolytes are completely ionised.

The question to be answered is why then should the equivalent conductance in such solutions of strong electrolytes vary with dilution. The conductance of a solution of a given electrolyte depends upon the number of ions and the speed with which the ions move. In the case of a solution of a strong electrolyte, the ionisation is complete, the number of ions will be the same, for 1 gm-equivalent will produce the same number of ions at all dilutions. Therefore, it is the speed of ions which changes with dilution. In a strong electrolyte, the density of ions is very high; every ion is surrounded by ions of opposite charge. The result is an interionic attraction between ions of opposite character. The ions may even give rise to some ion pairs of the type (A^+B^-) . Such interionic attraction effectively reduces the speed of the ions and hence the equivalent conductance of the solution. When concentration is lowered by increasing the dilution, the ions go far apart and the interionic forces are reduced. The ions would then move more freely. At infinite dilution, the interionic attraction practically disappears and the limiting value of the equivalent conductance is obtained. In a later section we shall show how a quantitative measure of the interionic attraction could be made. It is clear

that in the case of strong electrolytes, the Arrhenius concept of ionisation needs modification in as much as the degree of ionisation is no longer given by $\alpha = \lambda_c/\lambda_0$ for all the molecules are already ionised.

Weak Electrolytes. The equivalent conductance of weak electrolytes such as solutions of ammonia, organic fatty acids etc. is low at ordinary concentrations,

say 0.1 N. With dilution λ_c increases considerably as is shown by the plot of λ_c vs $\sqrt{c}$ (eqn. XII.18) for acetic acid in Fig. XII.8. It is seen that even when the concentration is made very small, the equivalent conductance rises steeply with dilution. As such it is not possible to reach a limiting value by extrapolation as in the case of strong electrolytes (cf. Fig. XII.7). Further dilution of the solution raises the resistance of the solution which is of the same order as that of water. So the experimental realisation of the limiting value of equivalent conductance at infinite dilution is not possible.

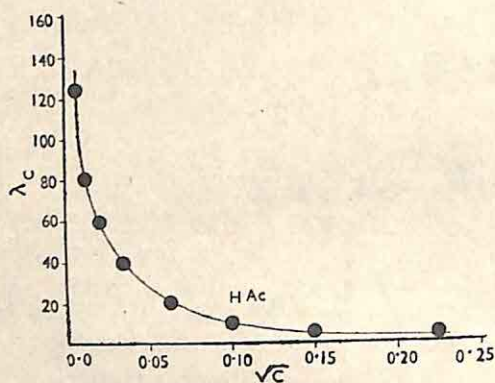


FIG. XII.8

In these electrolytes, the extent of ionisation is small and the numbers of ions are relatively few. So the interionic attraction between the ions is not of any importance. Whatever ions are produced by ionisation they are free to move, i.e., their speeds are not effected by interionic attraction. In solutions of ordinary concentration, the degree of ionisation is quite small. The increase in equivalent conductance with dilution is due to increase in the degree of ionisation. Therefore, the degree of dissociation (α) for weak electrolytes may be taken as the conductance ratio, $\alpha = \lambda_c/\lambda_0$, as proposed in the Arrhenius theory.

XII.11. Kohlrausch's Law of Independent Migration of Ions. While investigating the equivalent conductances at infinite dilution (λ_0). Kohlrausch found that when salts of potassium and sodium with a common anion are taken, the difference in their λ_0 -values was found to be same irrespective of the nature of the anion. That is, $\lambda_0^{\text{KCl}} - \lambda_0^{\text{NaCl}} = \lambda_0^{\text{KNO}_3} - \lambda_0^{\text{NaNO}_3} = \lambda_0^{\frac{1}{2}\text{K}_2\text{SO}_4} - \lambda_0^{\frac{1}{2}\text{Na}_2\text{CO}_4}$ etc., Similar results were also obtained with other pairs of salts having either a common anion or a common cation. A few of the results are shown below.

TABLE : λ_0 -VALUES FOR PAIRS OF ELECTROLYTES (25°C)

Electrolyte	λ_0	Difference $\lambda_{0(1)} - \lambda_{0(2)}$	Electrolyte	λ_0	Difference $\lambda_{0(1)} - \lambda_{0(2)}$
(1) KCl	149.9	21.1	(1) LiCl	115.0	4.9
(2) NaCl	128.8		(2) LiNO ₃	110.1	
(1) KNO ₃	145.0	21.1	(1) KCl	149.9	4.9
(2) NaNO ₃	123.9		(2) KNO ₃	145.0	
(1) KNO ₃	145.0	34.9	(1) HCl	426.16	4.9
(2) LiNO ₃	110.1		(2) HNO ₃	421.3	
(1) KClO ₄	140.0	34.92	(1) NaCl	128.8	4.9
(2) LiClO ₄	105.08		(2) NaNO ₃	123.9	
(1) KCl	149.9	34.9			
(2) LiCl	115.0				

Such a constancy in the difference of λ_0 -values of two salts having a common ion is possible only if each ion makes a definite contribution towards the conductivity of the solution irrespective of the value of the other ion. Thus,

$$\lambda_0(\text{NaCl}) = l_{0\text{Na}^+} + l_{0\text{Cl}^-} \text{ and } \lambda_{0\text{KCl}} = l_{0\text{K}^+} + l_{0\text{Cl}^-}, \text{ so that always}$$

$$\lambda_{0\text{KCl}} - \lambda_{0\text{NaCl}} = l_{0\text{K}^+} - l_{0\text{Na}^+},$$

whatever salts of sodium and potassium be taken, provided the salts are taken at infinite dilution with common anion.

Kohlrausch therefore proposed that at infinite dilution, each ion makes a definite contribution towards the equivalent conductance of the electrolyte. This contribution is independent of the other ion with which it is present in the solution. The value of the equivalent conductance at infinite dilution (λ_0) of an electrolyte is the sum of contributions of the two ions, such that

$$\lambda_0 = l_c^0 + l_a^0 \quad \dots (\text{XII.19})$$

where l_c^0 and l_a^0 are the contributions of the cation and anion respectively, called "ion conductances." That is, *at infinite dilution, the equivalent conductance is the sum of ion conductances*, which are characteristic of each ionic species. This is commonly known as the *law of independent migration of ions*.

The individual ionic conductances are usually determined from their transport number at infinite dilutions. At infinite dilution, an electrolyte is completely dissociated and there is no interionic attraction. In conveying a current, the conduction due to cations would depend upon their charge and their speed. In other words, ion conductance l_c^0 will depend upon charge (n_+z_+e) carried to the cathode and the speed u .

$$l_c^0 = k_1 n_+ z_+ e u$$

or

$$\text{Similarly for the anions contribution, } l_a^0 = k_1 n_- z_- e v$$

$\therefore$ From equation (XII.19),

$$\lambda_0 = l_c^0 + l_a^0 = k_1 n_+ z_+ e u + k_1 n_- z_- e v = ku + kv$$

$$\lambda_0 = k(u+v)$$

or

where $k = k_1 n_+ z_+ e = k_1 n_- z_- e$, the net charges released being equal.

$$\therefore \frac{l_c^0}{\lambda_0} = \frac{ku}{k(u+v)} = \frac{u}{u+v} \quad \dots (\text{XII.21})$$

Hence from equation (XII.7)

$$\frac{l_c^0}{\lambda_0} = t_+^0$$

$$\frac{l_a^0}{\lambda_0} = t_-^0$$

Similarly,

$$\text{i.e., } l_c^0 = t_+^0 \cdot \lambda_0; \text{ and } l_a^0 = t_-^0 \cdot \lambda_0 \quad \dots (\text{XII.23})$$

The zero-subscripts are used to indicate the state of infinite dilution in the application of these relations.

The transport numbers measured at low concentrations of an electrolyte are extrapolated to zero concentration to obtain t_+^0 and t_-^0 . The knowledge of the transport numbers (t_0) together with a determination of λ_0 would enable us to obtain the values of ion conductances (l^0). Some of ion conductance values are incorporated in the Table below.

TABLE : ION CONDUCTANCES AT INFINITE DILUTION (25°C)

Ion	l_+^0	Ion	l_-^0
H ⁺	349.8	OH ⁻	198.0
K ⁺	73.52	Cl ⁻	76.34
Na ⁺	50.11	Br ⁻	78.14
Ag ⁺	61.9	I ⁻	76.8
$\frac{1}{2}\text{Ca}^{++}$	59.5	NO ₃ ⁻	71.46
NH ₄ ⁺	73.4	$\frac{1}{2}\text{SO}_4^{--}$	80.0
$\frac{1}{2}\text{Mg}^{++}$	53.0	Ac ⁻	40.9

In the case of weak electrolytes, λ_0 , the conductance at infinite dilution cannot be directly obtained. In fact, the law of independent migration of ions is used for finding out λ_0 for weak electrolytes. To illustrate : λ_0 for acetic acid is evaluated by determining the equivalent conductances of three strong electrolytes separately, namely, HCl, NaCl and NaAc. It is easily seen

$$\begin{aligned}\lambda_{\text{HCl}}^0 + \lambda_{\text{NaAc}}^0 - \lambda_{\text{NaCl}}^0 &= (l_{\text{H}^+}^0 + l_{\text{Cl}^-}^0) + (l_{\text{Na}^+}^0 + l_{\text{Ac}^-}^0) - (l_{\text{Na}^+}^0 + l_{\text{Cl}^-}^0) \\ &= l_{\text{H}^+}^0 + l_{\text{Ac}^-}^0 = \lambda_{\text{HAc}}^0\end{aligned}$$

Since the quantities on the left-hand side are experimentally determined, λ_{HAc}^0 is known. This method is employed for other weak electrolytes also.

XII.12. Ionic Mobilities. The velocity of an ion in a solution depends upon the potential gradient applied. The velocity with which an ion would move under a potential gradient of 1 volt per centimeter in a solution is called its *ionic mobility*. The limiting value of the ionic mobility is obtained when the solution is at infinite dilution, so that no interionic attraction etc. would arise. The ionic mobilities are related to ion conductances.

From Kohlrausch's law we have seen, at infinite dilution ion conductances are proportional to their velocities, (eqn. XII.20).

$$\left. \begin{aligned} l_c^0 &= ku \quad \text{and} \quad l_a^0 = kv \\ \lambda_0 &= k(u+v) \end{aligned} \right\} \dots \text{(XII.20)}$$

and hence equivalent conductance,

Now suppose we have a very dilute solution of an electrolyte of concentration, C , such that there is complete dissociation. Take a cm-cube of this solution between two electrodes (1 cm apart, cross-section 1 sq. cm). Let the applied potential difference between the two electrodes be 1 volt, i.e., unit pot-gradient. The eqv. conductance of this solution is

$$\begin{aligned}\lambda_0 &= L_s \times \frac{1000}{C} \\ \text{or} \quad L_s &= \frac{C}{1000} \cdot (l_c^0 + l_a^0) \dots \text{(XII.24)}\end{aligned}$$

The current passing through the solution,

$$I = E/R = E \times \lambda = 1 \times L_s \quad (\text{since here } \lambda = L_s)$$

$$\text{or} \quad L_s = I \text{ (numerically).}$$

and I is the number of coulomb passing per unit time [voltage = 1 volt, and $t = 1$ second], i.e., the charge carried.

$$\therefore I = L_s = \frac{C}{1000} [l_c^0 + l_a^0] = \frac{C}{1000} \cdot k(u+v) \dots \text{(XII.25)}$$

Again, during this one second, all $+ve$ ions within a distance of u cms from the cathode and all $-ve$ ions within a distance v cms from the anode have reached the respective electrodes.

The total gm-equivalents of ions transported by the current to the two electrodes per sec would be

$$= u \times 1 \cdot \frac{C}{1000} + v \times 1 \cdot \frac{C}{1000} = \frac{C}{1000} \cdot (u+v)$$

$$[\text{remembering } \frac{C}{1000} \text{ gm-equivalent of ions are present in 1 c.c.}]$$

Since 1 gm-equivalent carries 1 faraday of electricity, the total charge carried

$$\text{per sec to the electrodes,} \quad = \frac{C}{1000} (u+v) \mathcal{F} \dots \text{(XII.26)}$$

Equating (XII.25 and 26), we have $\mathcal{F} = k$.

Hence, from (Eqn. XII.20) $l_c^0 = ku = \mathcal{F}u$

and $l_a^0 = kv = \mathcal{F}v$.

That is,

$$\left. \begin{aligned} u &= \frac{l_c^0}{\mathcal{F}} \\ v &= \frac{l_a^0}{\mathcal{F}} \end{aligned} \right\} \dots \text{(XII.27)}$$

The ionic mobilities are thus obtained by dividing the ion conductances by $\mathcal{F}$. The ionic mobility values of some common ions are tabulated here.

TABLE : IONIC MOBILITIES (25°C)

cation	$u \times 10^4$	anion	$v \times 10^4$
H ⁺	36.2	OH ⁻	20.5
K ⁺	7.61	SO ₄ ²⁻	8.27
Na ⁺	5.20	Cl ⁻	7.90
NH ₄ ⁺	7.60	Br ⁻	8.12
Ag ⁺	6.40	I ⁻	7.96
Ca ⁺⁺	6.16	NO ₃ ⁻	7.40
Mg ⁺⁺	5.50	Ac ⁻	4.25

Problem 4. Given the equivalent conductances of sodium butyrate, sodium chloride and hydrochloric acid as 83, 127 and 426 ohm⁻¹ cm² at 25°C respectively. Calculate the equivalent conductance of butyric acid at infinite dilution.

$$\begin{aligned} \lambda_{\text{HCl}} + \lambda_{\text{NaBu}} - \lambda_{\text{NaCl}} &= l_{\text{H}^+} + l_{\text{Cl}^-} + l_{\text{Na}^+} + l_{\text{Bu}^-} - l_{\text{Na}^+} - l_{\text{Cl}^-} \\ &= l_{\text{H}^+} + l_{\text{Bu}^-} = \lambda_{\text{HBu}} \end{aligned}$$

$$\therefore 426 + 83 - 127 = \lambda_{\text{HBu}} \text{ i.e., } \lambda_{\text{HBu}} = 382 \text{ ohm}^{-1} \text{ cm}^2$$

Problem 5. Calculate the ionic mobility of the cation in a 0.1 molar solution of NaCl at 25°C. Given its transference number as 0.39 and the equivalent conductance at infinite dilution as 127.

$$\text{We know, } t_c \cdot \lambda_0 = l_c^0 = u\mathcal{F}$$

$$\text{or } u = \frac{t_c \lambda_0}{\mathcal{F}} = \frac{0.390 \times 127}{96500} = 5.1 \times 10^{-4} \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$$

Problem 6. At 18°C, the mobilities of NH₄⁺ and ClO₄⁻ ions are 6.6×10^{-4} and 5.7×10^{-4} cm² volt⁻¹ sec⁻¹. Calculate equivalent conductance of ammonium chlorate and transport number of the two ions.

$$\begin{aligned} \text{We know } \lambda_0 &= \mathcal{F}(u+v) \\ &= 96500 [6.6 \times 10^{-4} + 5.7 \times 10^{-4}] = 118.7 \text{ ohm}^{-1} \text{ cm}^2 \end{aligned}$$

The transport number would be

$$t_c = \frac{l_c^0}{\lambda_0} = \frac{u\mathcal{F}}{\lambda_0} = \frac{u}{u+v} = \frac{6.6 \times 10^{-4}}{12.3 \times 10^{-4}} = 0.536$$

$$\therefore t_a = 1 - 0.536 = 0.464$$

XII.12a. Temperature and Ionic Conductances. In aqueous solutions, the ionic conductance generally increases with temperature. An empirical relation is given as

$$l_t^0 = l_{25}^0 [1 + 0.02(t - 25)] \dots \text{(XII.28)}$$

where t is expressed in °C. It means for every degree rise in temperature, the ionic conductance approximately increases by 2%. This is really due to the fall in viscosity of the medium due to temperature-rise. For H⁺ and OH⁻ ions, the change of l^0 is somewhat less.

XII.13. Hydration of Ions. Ion conductances can be obtained from measurement of transport numbers and equivalent conductivity at infinite dilution, for

$$l_c = t_c \lambda_0 \quad \text{and} \quad l_a = t_a \lambda_0$$

When the ion conductances of the cations of different alkali chlorides at a given concentration were measured it was found that the ion conductance of the cations systematically increased with atomic weight from lithium to caesium.

Ion	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
l_c	38.6	50.1	73.5	77.8	77.8

Now the ion conductance depends upon the charge and the speed of the ions. In these cases, the anion is the same, every cation carries unit charge, hence the low ion conductance of Li⁺ or Na⁺ ion is obviously due to their lesser speed. This is however contrary to expectation, for, normally the lighter and smaller Li⁺ ion is expected to move faster than the heavier ions (say) K⁺ or Rb⁺ ions under a given potential gradient. That the lithium ion is smaller is known from its atomic structure as also established from X-ray diffraction measurements of its crystalline compounds. It is therefore reasonably assumed that the low speed of ions is due to the fact that the ions are not *bare* but hydrated. Further, the degree of hydration decreases with increase in atomic weight. The lithium ion being small the electric field in its neighbourhood is much stronger than that in the case of K⁺ ion or Cs⁺ ion. So a lithium ion is capable of attracting or associating with a larger number of water molecules than a potassium or caesium ion can. The net result is that the hydrated Li⁺ ion has a larger dimension than other alkali cations.

Taking the cation to be a sphere of radius r_+ we can apply Stoke's law when it moves through the medium with a velocity v under a potential E . The frictional force, $f = 6\pi r_+ \eta v$, is balanced by the electrical force eE . That is,

$$6\pi r_+ \eta v = \frac{eE}{300} \quad [\text{the factor 300 is used for conversion into volts}]$$

$$\text{Now} \quad l_c = \frac{v}{E} \mathcal{F} = \frac{e\mathcal{F}}{300 \times 6\pi r_+ \eta}$$

$$\text{or} \quad r_+ = \frac{e\mathcal{F}}{l_c \times 300 \times 6\pi \eta}$$

As l_c has been experimentally observed to be smaller in the case of lithium ion, its effective radius must be greater than those of Na⁺, K⁺ or other alkali cations.

How the hydration or solvation of the ions occur is not quite clear; it may be the solvent molecules are held by purely physical forces or there may be chemical solvation through co-ordinate linkage. In the case of H⁺ ion in aqueous solutions, it is generally held that chemical hydration (H₃O⁺) occurs. Even when chemical solvation occurs, it is generally accepted that solvent molecules may also remain attached to the ions by electrostatic forces depending on the dipole character of the solvent and the intensity of charges on the ion surface.

When a cation moves, under a potential, towards the cathode it carries with it some water from the anode to the cathode compartment. Similarly, if anions are also hydrated, these would bring to the anode compartment an amount of water. As a result there would be concentration changes in the two compartments. The transport number determined by Hittorf method is really that of the hydrated ion and an apparent one; it is not the transport number of the ion itself.

Let t_c and t_a denote the true transport number of cation and anion, where t'_c and t'_a represent the experimentally determined apparent transport numbers. Suppose each cation and anion are hydrated with q_+ and q_- molecules of water. When one faraday of electricity is passed, the anode compartment loses $q_+ t_c$ moles of water and gains $q_- t_a$ moles of water. There is hence a net transfer of (say) x moles of water from the anode compartment. That is

$$x = (q_+ t_c) - (q_- t_a) = (q_+ t_c) - [q_- (1 - t_c)] \quad \dots (i)$$

Further suppose initially w_s gm-equivalent of salt was present in W moles of water. The transfer of x moles of water raises the concentration of salt by an amount $x.w_s/W$ gm equivalents in the anode chamber. That is, the loss in conc. of cations in the anode compartment is less than what it should have been if water were not transported. Now the transport number of cation is proportional to the loss of cations from the anode chamber. The apparent transport number experimentally obtained (t'_c) will hence be less than the true transport number (t_c) by an amount $x.w_s/W$.

$$\text{or} \quad t_c - t'_c = x \frac{w_s}{W} \quad \dots (ii)$$

It was Washburn (1909) who first succeeded in estimating x , the moles of water transported by an ion. He added a reference non-electrolytic substance raffinose to the electrolyte. Raffinose would not migrate when electricity is passed. The change in its concentration was measured from optical rotation values. The water transferred (x) was thus known. Subsequently other substances, such as urea, were also used. With the knowledge of x , it is possible to evaluate the true transport number t_c from equation (ii). Again, from equation (i) we have,

$$q_+ = (x + q_-)/t_c - q_-$$

The hydration number of cation q_+ can be obtained only if a value for q_- is assumed or *vice versa*. Farther it was believed that the chloride ion is hydrated with 4-molecules of water, i.e., $q_- = 4$. On this assumption, the hydration numbers of alkali cations were : Li^+ 14, Na^+ 8.4, K^+ 5.4... etc. But it is now generally agreed that the negative ions are scarcely hydrated ($q_- = 0$). On this basis, the hydration numbers are

$$\text{Li}^+ 6, \text{Na}^+ 4, \text{K}^+ 2, \text{Rb}^+ 1, \text{Cs}^+ 1.$$

XII.14. The Interionic-Attraction Theory. We have seen that strong electrolytes are considered as completely ionised in solution, which means that in a solution containing 1 gm-equivalent the number of ions would be the same at all concentrations. And yet the equivalent conductance increases with dilution. This is due to the change in the other factor, namely ionic speed, which alters with dilution. At ordinary concentration, the ions are in close proximity and hence there are interionic forces which render them unable to move with a speed as would otherwise be possible. With dilution, the interionic forces diminish and hence the conductance increases.

In 1923, Debye and Hückel treated the interionic effects for a solution carrying an electric current quantitatively. This is known as *Debye-Hückel theory of interionic attraction*. The treatment was later modified in some respects by Lars Onsager (1927). It is based on the application of the laws of hydrodynamics and the mathematical presentation is highly involved. We shall only describe here briefly a qualitative account of the different forces which influence the speed of an ion in solution moving under an applied electric field.

Let us consider an ion in a solution, say a representative positive ion of charge e , which we shall name as the central ion. Let E be the intensity of the external electric field which directs the ion to move in the direction of x -axis. There are really four different forces which play on the given ion and we may consider them separately.

1. Firstly, there is the electric force Ee acting on the ion in the direction of the x -axis.

2. Secondly, as the ion moves forward, there is a frictional force which retards its motion ; this is the viscous force. If the velocity of the ion be v in the x -direction and the medium is assumed to be at rest, the frictional force would be

$$f = -kv$$

i.e.,

$$f = -6\pi\eta rv \text{ (By Stokes law)}$$

when η is the viscosity of the medium and r is the radius of the ion assumed to be spherical.

This leads to another interesting result, for the frictional force would be counterbalanced by the electrical force and hence

$$6\pi r\eta v(\times 300) = Ee$$

expressing E in volts.

$$\text{Hence the mobility of the ion} = \frac{v}{E} = \frac{e}{6\pi r\eta \times 300} = \frac{k_1}{r\eta}$$

The equivalent conductance of the solution then,

$$\lambda_0 = (I_c + I_a) = \mathcal{F}(u+v) = \frac{k_1 \mathcal{F}}{\eta} \left[\frac{1}{r_c} + \frac{1}{r_a} \right]$$

$$\text{or } \lambda_0 \times \eta = \text{constant, for a specified electrolyte} \quad \dots (XII.29)$$

This is *Walden's rule*. The determination of $(\lambda_0\eta)$ for a given electrolyte in different solvents did not prove quite satisfactory except when the ions are large and hence solvation is less. Due to solvation the effective radius of an ion is much different from r_+ and r_- of the unsolvated ion. When the ions are large the electric field of the ion is weaker, the solvation is less and the effective radius in different solvents is nearly the same. In such circumstances, Walden's rule is valid.

3. Thirdly, in the Debye-Hückel theory it is conceived that each ion is surrounded by an ionic atmosphere whose net charge is on the average opposite to that of the central ion. Thus if the central ion is a positive one, there would be other ions surrounding it where the net charge would be negative. Similarly a negative central ion would have a positive ionic atmosphere. In the absence of an external applied field, the ionic atmosphere is spherically and symmetrically disposed about the central ion, so that it exerts no net force on the ion (Fig. XII.9a). When an external force is applied such as the potential across two electrodes immersed in solution the ion moves in one direction (say x -axis), but the ionic atmosphere does not have time to adjust itself to remain spherically distributed around the central ion and it lags behind (Fig. XII.9b). As a consequence the ion is retarded in its motion by the atmosphere, for the negative charges behind would be greater than those in front of the central ion. This force causing retardation will be in a direction opposite to that of the motion of the central ion. The ionic atmosphere during the motion of the central ion becomes unsymmetrical. This effect on the velocity of an ion is called the *asymmetry effect or relaxation effect*. The density of negative charge at any point in the ionic atmosphere surrounding a central positive ion depends upon the distance ' r ' of the point from the central ion. The effect of the ionic atmosphere decreases when r is large, i.e., when the atmosphere is far away. Moreover when the dielectric constant of the solvent is large, the force between the ions is reduced and hence the effect of ionic atmosphere also is less. Onsager

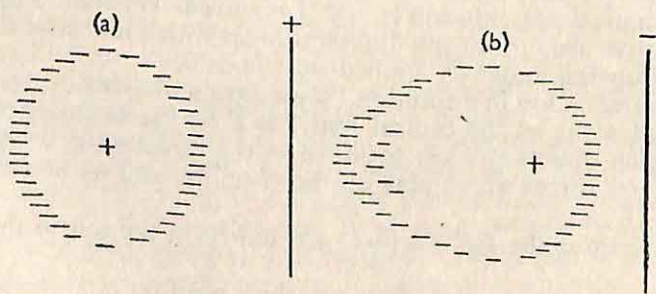


FIG. XII.9

calculated, in terms of ionic charges, concentration of the solution, dielectric constant of the solvent and temperature, the force which opposes the motion of the central ion. He found that this may be expressed as $-k_1 E \sqrt{C}$; the magnitude of k_1 depends upon η , T and r .

4. There is still another force which opposes the speed of an ion and is responsible for lowering the conductivity. This arises out of *electrophoretic effect*.

The concept of the ionic atmosphere also presumes that in the neighbourhood of a central positive ion the solvent contains more negative than positive charges. When an external field is applied, the +ve ions move in the direction of x -axis whereas the negative ions would move in the opposite direction. The ions during their motion would impart momentum to the solvent molecules. Since -ve charges are in excess, the net momentum imparted to the solvent will be in the direction of the negative x -axis. In short, a 'streaming' of the solvent in a direction opposite to that of the motion of central ion would occur. In other words the relative velocity of the ion would be greater than that assigned to the ion assuming the solvent to be stationary. The streaming of the solvent due to the application of the electric field is called *electrophoresis*. In item 2 of this section we found the viscous force to be $-k\nu$ where ν was taken as relative velocity when solvent was regarded as stationary. The actual value of ν will be higher. There is thus an additional frictional force in consequence of electrophoresis. Debye and Hückel as also Onsager expressed this opposing force due to electrophoretic effect as $-k_2 E \sqrt{C}$

Under equilibrium conditions, the four forces may be equated as

$$Ee = k\nu + k_1 E \sqrt{C} + k_2 E \sqrt{C}$$

or
$$\nu = \frac{Ee}{k} - \frac{k_1 + k_2}{k} E \sqrt{C}$$

It is easily seen that due to the presence of the ionic atmosphere and in consequence of the asymmetric, the electrophoretic and viscous effects, the mobility of an ion in a solution of concentration C would be less than that in an infinitely dilute state, $Lt.C \rightarrow 0$.

The ultimate mathematical form for the expression of equivalent conductance of a dilute solution of concentration C was given by Onsager as

$$\lambda = \lambda_0 - \left[\frac{0.9834 \times 10^6}{(DT)^{\frac{3}{2}}} \omega \lambda_0 + \frac{28.94(z_1 + z_2)}{\eta(DT)^{\frac{1}{2}}} \right] \sqrt{(z_1 + z_2)C}$$

The symbol $\omega = \frac{2q}{1 + \sqrt{q}} z_1 z_2$ where $q = \frac{z_1 z_2 (l_c^0 + l_a^0)}{(z_1 + z_2)(z_1 l_c^0 + z_2 l_a^0)}$

z_1, z_2 are the valences of the two ions, D is the dielectric constant of the medium, η , the viscosity coefficient. This relation is deduced for strong electrolytes in which ionisation is complete and even then it is valid in the case of solutions of appreciably low concentration. When the electrolyte is a uni-univalent one, Onsager's equation takes the form,

$$\lambda = \lambda_0 - \left[\frac{82.4}{(DT)^{\frac{1}{2}} \eta} + \frac{8.20 \times 10^5}{(DT)^{\frac{3}{2}}} \lambda_0 \right] \sqrt{C} \quad \dots \text{(XII.30)}$$

The first term within the paranthesis is due to electrophoretic effect and the second term due to asymmetry effect.

For a given solvent at a constant temperature, we may write the equation as,

$$\lambda = \lambda_0 - [A + B \lambda_0] \sqrt{C} \quad \dots \text{(XII.31)}$$

A and B replace the constant quantities within the bracket of equation (XII.30). In aqueous solution at 25°C, $A = 60.2$ and $B = 0.229$.

It is obvious that the plot of $\lambda \sqrt{C}$ at low concentration would be a straight line. For a number of uni-univalent electrolytes this has been found to be true as

in Fig. (XII.10). This confirms that the basic assumptions made in the theory are sound and correct. The slope of the lines in the curves would give the value of $A + B\lambda_0$, and the intercept the value of λ_0 .

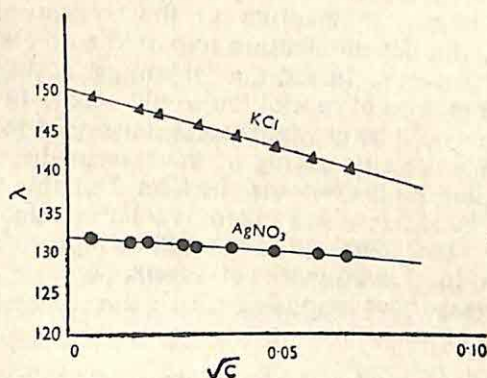


FIG. XII.10

XII.15. Some Simple Applications of Conductance Measurement. The determination of conductance of solutions enables us to find out some valuable data about the electrolyte. A few of these are illustrated here.

(i) **Degree of Dissociation of Weak Electrolytes.** Even in fairly dilute solutions, weak electrolytes are dissociated to a small extent. The number of ions being small, the effect of interionic attraction (Onsager) is negligible for practical purposes. As such the velocities of the ions of weak electrolytes at a definite concentration and at infinite dilution are the same. With dilution, the extent of dissociation increases and hence the number of ions increase. The increase in equivalent conductance is thus due to rise in the degree of dissociation.

Suppose a gm-equivalent of the electrolyte at infinite dilution produces n_+ positive and n_- negative ions whose valences are z_+ and z_- . Then, at infinite dilution, the eqv. conductance would be

$$\lambda_0 = n_+ z_+ eu + n_- z_- ev \quad \dots (a)$$

e = unit charge, u and v are the velocities of the ions.

If α be assumed to be the degree of dissociation at a given concentration (C) of the solutions, the equivalent conductance would be

$$\lambda = \alpha n_+ z_+ eu + \alpha n_- z_- ev \quad \dots (b)$$

αn_+ and αn_- are the number of ions at concentration (C).

Dividing (b) by (a),

$$\alpha = \frac{\lambda}{\lambda_0} \quad \dots (XII.32)$$

In other words, the weak electrolytes obey the basic postulates of Arrhenius theory.

We have seen that eqv. conductance at infinite dilution is the sum of the ion conductances, $\lambda_0 = l_c^0 + l_a^0$, hence

$$\alpha = \frac{\lambda}{l_c^0 + l_a^0} \quad \dots (XII.33)$$

This relation is universally employed to find out the degree of dissociation of weak electrolytes.

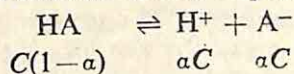
Problem 7. The equivalent conductance of a 0.014 N solution of chloracetic acid is 109.0. The ion conductances of chloracetate and hydrogen ions are 40.2 and 349.8 respectively. Calculate the degree of dissociation.

$$\lambda_0 = 349.8 + 40.2 = 390.0$$

Hence

$$\alpha = \lambda / \lambda_0 = 109 / 390 = 0.48$$

(ii) **Dissociation Constants of Weak Acids.** The ions produced on dissociation are in equilibrium with the undissociated molecules of weak electrolytes in solution. Thus a weak acid solution of HA will have the equilibrium,



C is the concentration and α , the degree of dissociation. Applying the Law of Mass Action, the eqm. constant better known as dissociation constant of the acid, is given by

$$K_a' = \frac{C_{\text{H}^+} \times C_{\text{A}^-}}{C_{\text{HA}}} = \frac{\alpha C \times \alpha C}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha} \quad \dots \text{(XII.34)}$$

Now $C = \frac{1}{v}$, where v is the volume of the solution,

$$\text{therefore,} \quad K_a' = \frac{\alpha^2}{v(1-\alpha)} \quad \dots \text{(XII.34a)}$$

$$\text{Again } \alpha = \frac{\lambda}{\lambda_0}, \text{ so } K_a' = \frac{(\lambda/\lambda_0)^2 C}{(1-\lambda/\lambda_0)} = \frac{\lambda^2 C}{\lambda_0(\lambda_0 - \lambda)} \quad \dots \text{(XII.35)}$$

Thus a determination of λ and knowledge of $l_{\text{H}^+}^0$ and $l_{\text{A}^-}^0$ would enable the evaluation of dissociation constant.

In Problem 7 mentioned above, the equivalent conductance $\lambda = 109$ and $\lambda_0 = 390$. Hence, the dissociation constant of chloracetic acid would be,

$$K_a' = \frac{\lambda^2 C}{\lambda_0(\lambda_0 - \lambda)} = \frac{(109)^2 \times (0.014)}{390(390 - 109)} = 1.5 \times 10^{-3}$$

The use of these formulae gives only approximate values as in applying the equilibrium the concentration terms have been used and not the activities. We shall see later a more accurate method for the determination of the dissociation constant.

When the degree of dissociation (α) is very small, we can write the equation (XII.34) approximately as

$$K_a' \approx \alpha^2 C, \text{ i.e., } \alpha = \sqrt{K_a'/C} \quad \dots \text{(XII.36)}$$

i.e., in the case of very weak electrolytes, the degree of dissociation at a given concentration is proportional to the square root of the dissociation constant. (Sec. XII.20).

Problem 8. Find out the degree of dissociation and the hydrogen ion concentration at 25°C for a 0.01 molar solution of propionic acid ($K_a' = 1.32 \times 10^{-5}$).

Since the acid is a very weak one, we can apply equation (XII.36), i.e.,

$$\alpha = (K_a'/C)^{\frac{1}{2}} = (1.32 \times 10^{-5}/0.01)^{\frac{1}{2}} = 0.0363.$$

The concentration of hydrogen ions = $0.01 \times 0.0363 = 3.63 \times 10^{-4}$ gm.-eq./litre.

(iii) **Degree of Dissociation of Water.** Water conducts very feebly, but nevertheless even the purest form of water obtained after repeated careful distillation is slightly dissociated and behaves as a very weak electrolyte. The specific conductance of pure water at 25°C has been found to be 0.58×10^{-7} ohm⁻¹ cm⁻¹.

Hence, the eqv. conductance of water is $\lambda = \frac{L \times 1000}{C}$

$$\begin{aligned} \text{or} \quad \lambda &= (0.58 \times 10^{-7}) \cdot V_m, \quad (V_m, \text{ molar volume}) \\ &= (0.58 \times 10^{-7}) \times \frac{18}{0.997} = 1.05 \times 10^{-6}, \quad (d = 0.997) \end{aligned}$$

Its eqv. conductance on complete dissociation would be

$$\lambda_0 = l_{\text{H}^+} + l_{\text{OH}^-} = 349.8 + 198 = 547.8$$

$\therefore$ The degree of dissociation of water at 25°C

$$\alpha = \frac{\lambda}{\lambda_0} = \frac{1.05 \times 10^{-6}}{547.8} = 1.9 \times 10^{-9}$$

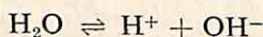
And the conc. of H^+ ions, $C_{H^+} = a.C = 1.9 \times 10^{-9} \times 1000/18$.

$$= 1.05 \times 10^{-7} \text{ gm-equivalents per litre}$$

In pure water the concentrations of H^+ and OH^- ions are equal, $C_{H^+} = C_{OH^-}$. The product of the concentrations of the two ions is called *ionic product of water* universally represented as k_w ; its value at $25^\circ C$,

$$k_w = C_{H^+} \times C_{OH^-} = (1.05 \times 10^{-7})^2 = 1 \times 10^{-14} \quad \dots \text{(XII.37)}$$

It may be noted that k_w is the *ionic product* of water and not the dissociation constant of the process.



$$\begin{aligned} \text{The dissociation constant, } K_{H_2O} &= \frac{C_{H^+} \times C_{OH^-}}{C_{H_2O}} = \frac{C_{H^+}^2}{C_{H_2O}} \\ &= \frac{(1.05 \times 10^{-7})^2}{1000/18} = 1.8 \times 10^{-16} \end{aligned}$$

assuming the conc. of undissociated H_2O as constant.

(iv) **Basicity of Organic Acids.** As early as in 1887, Ostwald from his study of conductivities of solutions of aliphatic organic acids suggested empirically a relation expressed as

$$\lambda_{1024} - \lambda_{32} = (10.8)b$$

where λ_{1024} and λ_{32} are the equivalent conductances of the acid at dilution of 1024 and 32 litres and b is the basicity of the acid. The relation however is not applicable in the case of inorganic acids except in some per-acids.

(v) **Determination of Solubilities of Sparingly Soluble Salts.** The saturated solutions of sparingly soluble salts like $BaSO_4$, $AgCl$, etc. have extremely low concentrations. These solutions may be regarded as at infinite dilution. If the specific conductance of such a solution be L_s and that of water used for making the solution L_{H_2O} , then the equivalent conductance would be

$$\lambda = (L_s - L_{H_2O}) \cdot \frac{1000}{S}$$

where S is the solubility (or conc.) in gm-equivalent of the salt. A correction for conductance of water is introduced here as L_s is quite low.

But here,

$$\lambda = \lambda_0 = l_c^0 + l_a^0$$

Therefore,

$$S = \frac{(L_s - L_{H_2O}) \times 1000}{l_c^0 + l_a^0} \quad \dots \text{(XII.38)}$$

Problem 9. The specific conductance of $SrSO_4$ in a saturated solution at $25^\circ C$ is 1.5×10^{-4} and that of water $1.5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$, what is the solubility of this salt at $25^\circ C$?

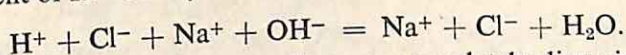
Using equation (XII.38).

$$\text{Solubility } S = \frac{(150 \times 10^{-6} - 1.5 \times 10^{-6}) \times 1000}{(59.2 + 79.8)}$$

$$\begin{array}{l} \therefore l_{Sr^{++}} = 59.2 \\ l_{SO_4^{--}} = 79.8 \\ \text{eq. wt. of } SrSO_4 = 92.8 \end{array} \quad \left| \begin{array}{l} = 1.07 \times 10^{-3} \text{ gm-eqv. per litre} \\ = 92.8 \times 1.07 \times 10^{-3} = 0.099 \text{ gms/litre.} \end{array} \right.$$

(vi) **Conductometric Titrations. (a) Acid-Base Titrations.** When an acid is titrated with a base, the conductance of the resulting solution varies with every addition of titre. As a simple illustration let us take the titration of a strong acid, say hydrochloric acid, by a strong base, say caustic soda. The titration is to be

carried out in a conductivity bottle as shown in Fig. XII.11. The base, whose conc. should be much higher than the acid taken in the bottle in order to avoid any large dilution effect, is added slowly in small lots from a microburette. The bottle should be kept in a thermostat. The conductance is measured after each addition of the titre caustic soda. The neutralisation in this process would really mean the replacement of H^+ ions by Na^+ ions in equal numbers :



Since HCl and $NaOH$ are both strong, these are completely dissociated. When any reaction occurs, some H^+ ions will disappear along with OH^- ions and in the solution Na^+ ions will remain. The ionic conductance of H^+ ion is much higher than that of Na^+ . The result is that the conductance of the solution will decrease as more and more $NaOH$ are added, as shown in Fig. XII.12a. $1/R$ vs vol. of titre. In this way all the H^+ ions are removed, the conductance would reach the lowest point. Further addition of $NaOH$ means increase in the number of ions both Na^+ ions and also relatively faster moving OH^- ions. These are no longer removed and hence the conductance would rise again linearly with addition of titre. The point of intersection of the two lines, i.e., the lowest point, corresponds to the minimum conductance which is the exact neutralisation point. It is not necessary to find out the conductance at the exact neutralisation point. Some three or four measurements on either side of the minimum point would give on extension the point of intersection.

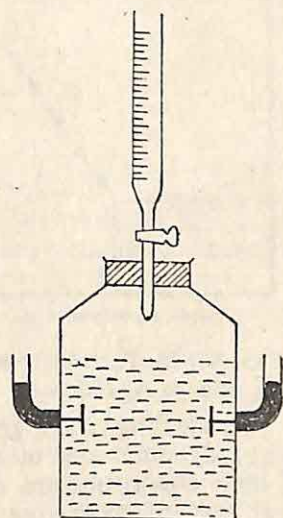


FIG. XII.11 Conductivity bottle for titrations

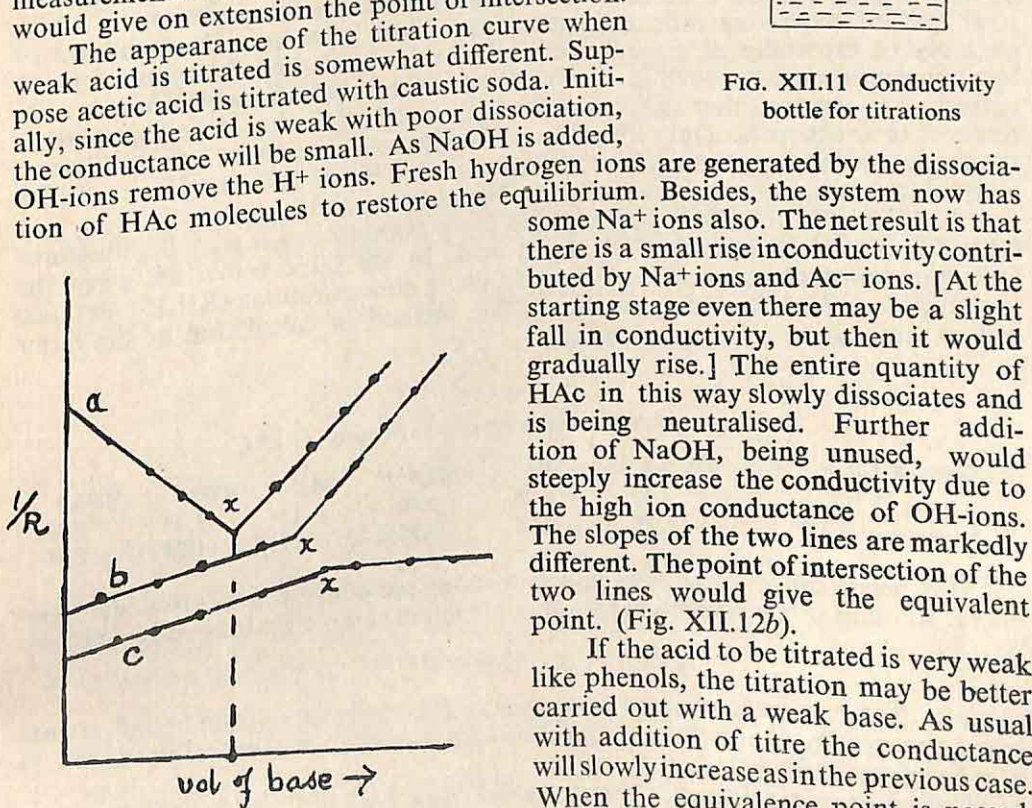


FIG. XII.12 Acid-base Conductometric Titration Curves (x, equivalence point).

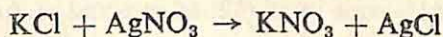
(a) Strong acid Vs. Strong base (b) Weak acid Vs. Strong base (c) Weak acid Vs. Weak base

The appearance of the titration curve when weak acid is titrated is somewhat different. Suppose acetic acid is titrated with caustic soda. Initially, since the acid is weak with poor dissociation, the conductance will be small. As $NaOH$ is added, OH^- ions remove the H^+ ions. Fresh hydrogen ions are generated by the dissociation of HAc molecules to restore the equilibrium. Besides, the system now has some Na^+ ions also. The net result is that there is a small rise in conductivity contributed by Na^+ ions and Ac^- ions. [At the starting stage even there may be a slight fall in conductivity, but then it would gradually rise.] The entire quantity of HAc in this way slowly dissociates and is being neutralised. Further addition of $NaOH$, being unused, would steeply increase the conductivity due to the high ion conductance of OH^- ions. The slopes of the two lines are markedly different. The point of intersection of the two lines would give the equivalent point. (Fig. XII.12b).

If the acid to be titrated is very weak like phenols, the titration may be better carried out with a weak base. As usual with addition of titre the conductance will slowly increase as in the previous case. When the equivalence point is passed, further addition of weak base will not materially change the conductance, the line will be almost parallel to the volume axis. This is indicated in Fig. (XII.12c).

Such conductometric titrations are often most convenient, when use of indicators becomes impossible or unsuitable, as in coloured solutions or in very weak acids or bases.

(b) **Precipitation Reactions.** Reactions in which precipitates are readily formed can also be followed conductometrically. In a reaction of the type,



we have really $\text{K}^+ + \text{Cl}^- + \text{Ag}^+ + \text{NO}_3^- \rightarrow \text{K}^+ + \text{NO}_3^- + \text{AgCl}$. That is, on addition of the titre AgNO_3 , the K^+ ions remain unchanged in amount, the Cl^- ions are substituted by NO_3^- ions. The ion conductances of Cl^- and NO_3^- ions are not much different. Hence, the conductance of the solution with successive addition of AgNO_3 will not alter much, the line would remain parallel to the axis of precipitant volume, as in Fig. (XII.13). When the equivalence point is passed, there will be a sharp rise in conductance as unused Ag^+ and NO_3^- are added. The end-point of the reaction (the point of intersection of the lines) can be determined quite easily.

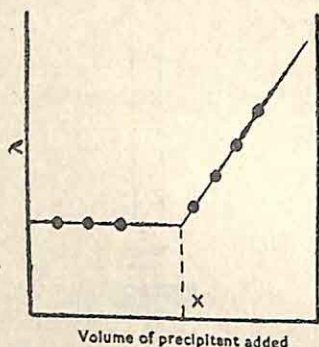


FIG. XII.13. Titration of KCl soln. by AgNO_3 soln.

XII.16. Activities in Electrolytic Solutions. In Chapter IV, Section IV.60, the terms activity and activity coefficients have been defined and their relations to concentrations have been generally explained.

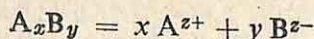
In dealing with gaseous systems and solutions of non-electrolytes, their thermodynamic and other properties can be fairly accurately expressed in terms of their concentrations even at moderate concentrations (or pressures). That is, such systems have very little departure from ideal behaviour. But solutions of electrolytes, especially of strong electrolytes, exhibit marked deviations even at low concentrations. As such in the treatment of reactions in which ions are involved, it is essential that their equilibria, kinetics, etc. should be expressed in terms of their activities. Only when the electrolyte solutions are at infinite dilution, the concentration terms can substitute the activities, for, in such conditions activity is equal to concentration, the activity coefficient being unity.

That the use of activity terms yields more accurate result may be illustrated from the ionisation constants of acetic acid. In the table below are given the ionisation constant values (k') of the acid using concentrations (XII.35) and also ionisation constant (k) using activities. The method of calculation of the latter will be shown in a subsequent section.

TABLE : IONISATION CONSTANTS OF ACETIC ACID AT 25°C

Conc. $\times 10^5$	2.8	21.8	102.8	984.0	2000.0	5000.0
$k'(\text{conc}) \times 10^5$	1.77	1.78	1.80	1.83	1.84	1.85
$k(\text{activities}) \times 10^5$	1.75	1.75	1.75	1.75	1.74	1.74

It is necessary to know how concentrations are converted to activities. Consider a solution of an electrolyte ($\text{A}_x \text{B}_y$) which is completely ionised in solution.



where z_+ and z_- are the charges of the ions. The subscripts $+$ and $-$ will always refer to properties of positive and negative ions; symbols without subscript would refer to neutral molecules.

If there are c molecules of the electrolyte dissolved in the c_s molecules of solvent, then thermodynamic potential of the solution would be sum of the thermodynamic potentials of solvent and the ions, i.e.,

$$G = c_s \mu_s + c[x \mu_+ + y \mu_-] \quad \dots (A)$$

μ -terms are the respective chemical potentials.

$$\text{We also have } G = c_s \mu_s + c \mu \quad \dots (B)$$

where μ is the chemical potential of the electrolyte in solution.

$$\text{Comparing (A) and (B) } \mu = x\mu_+ + y\mu_- \quad \dots (C)$$

Let $v = x + y$, the total number of ions produced from 1 molecule. And if $\mu_{\pm}$ is the mean ionic chemical potential, then

$$v\mu_{\pm} = x\mu_+ + y\mu_- \quad \dots (D)$$

$$\therefore \mu = v\mu_{\pm} \quad \dots (E)$$

Now these chemical potentials may be expressed in the formal way (eqn. IV.121),

$$\left. \begin{aligned} \mu_+ &= \mu_+^{\circ} + RT \ln a_+ \\ \mu_- &= \mu_-^{\circ} + RT \ln a_- \\ \mu_{\pm} &= \mu_{\pm}^{\circ} + RT \ln a_{\pm} \\ \mu &= \mu^{\circ} + RT \ln a \end{aligned} \right\} \quad \dots (F)$$

where a_+ and a_- are the activities of the ions, a is the activity of the electrolyte in solution, $a_{\pm}$ is the mean ionic activity. Moreover under standard states, by definition,

$$\begin{aligned} \mu^{\circ} &= x\mu_+^{\circ} + y\mu_-^{\circ} \\ v\mu_{\pm}^{\circ} &= x\mu_+^{\circ} + y\mu_-^{\circ} \\ \therefore \mu^{\circ} &= v\mu_{\pm}^{\circ} \end{aligned} \quad \dots (G)$$

Substituting (F) in (E), $\mu^{\circ} + RT \ln a = v\mu_{\pm}^{\circ} + vRT \ln a_{\pm}$

$$\text{i.e., } a = a_{\pm}^v \quad \dots (\text{XII.39})$$

Again, substituting equation (F) in (D), we have,

$$v\mu_{\pm}^{\circ} + vRT \ln a_{\pm} = x\mu_+^{\circ} + y\mu_-^{\circ} + xRT \ln a_+ + yRT \ln a_-$$

$$\text{i.e., } a_{\pm}^v = a_+^x \cdot a_-^y \quad \dots (\text{XII.40})$$

$$\text{or } a_{\pm} = \sqrt[v]{a} = \sqrt[v]{a_+^x \cdot a_-^y} \quad \dots (\text{XII.41})$$

The mean ionic activity is the geometric mean of the individual ion activities.

Using formal expressions between activity and concentration, we may also write,

$$\left. \begin{aligned} a &= fC, \\ a_{\pm} &= f_{\pm} C_{\pm} \\ a_+ &= f_+ C_+ \\ a_- &= f_- C_- \end{aligned} \right\} \quad \dots (H)$$

in which f -terms are the activity coefficients and C -terms are the concentrations in molar units.

Introducing equation (XII.41),

$$a = a_+^x \cdot a_-^y = (f_+ C_+)^x (f_- C_-)^y = (C_+^x \cdot C_-^y) \cdot f_+^x \cdot f_-^y \quad \dots (\text{XII.42})$$

$$\text{and hence } a_{\pm} = (C_+^x \cdot C_-^y)^{\frac{1}{v}} \cdot (f_+^x f_-^y)^{\frac{1}{v}} \quad \dots (\text{XII.43})$$

Aided by relations in (H), we define

$$\text{mean activity coefficient of the electrolyte, } f_{\pm} = (f_+^x \cdot f_-^y)^{\frac{1}{v}}$$

$$\text{and mean molarity of the electrolyte, } C_{\pm} = (C_+^x \cdot C_-^y)^{\frac{1}{v}}$$

$$\begin{aligned} \text{Thus, } a_{\pm} &= a^{\frac{1}{v}} = C_{\pm} \cdot f_{\pm} \\ \text{and } a &= a_{\pm}^v = (C_{\pm} \cdot f_{\pm})^v \end{aligned} \quad \dots (\text{XII.44})$$

If we consider a solution of molarity C , then

$$C_+ = xC; C_- = yC.$$

So

$$a_{\pm} = \sqrt[v]{a} = [(xC)^x(yC)^y]^{\frac{1}{v}} f_{\pm}$$

$$= (x^x y^y)^{\frac{1}{v}} C f_{\pm}$$

$$a = (x^x y^y) C^v f_{\pm}^v$$

and

... (XII.45)

These expressions correlates concentration and activity.

For a uni-univalent type of electrolyte, $x = 1, y = 1, x + y = v = 2$,

$$\text{hence } a_{\pm} = (1 \times 1)^{\frac{1}{2}} C f_{\pm} = C f_{\pm}$$

and

$$a = a_{\pm}^2 = C^2 f_{\pm}^2$$

For a uni-bivalent type (say BaCl_2), $x = 1, y = 2, v = 3$,

$$\text{hence } a_{\pm} = (1 \times 2^2)^{\frac{1}{3}} C f_{\pm} = \sqrt[3]{4} \cdot C f_{\pm}$$

and

$$a = a_{\pm}^3 = 4C^3 f_{\pm}^3$$

For some simple electrolytes, the expression for $a_{\pm}$ and a are given below.

TABLE : EXPRESSIONS FOR $a_{\pm}$ AND a FOR DIFFERENT ELECTROLYTES

Electrolyte	type	x, y	v	$C_{\pm}$	$a_{\pm}$	$a (= a_{\pm}^v)$
$\text{NaCl}, \text{ZnSO}_4$ etc.	1-1	1, 1	2	C	$C f_{\pm}$	$C^2 f_{\pm}^2$
$\text{CaCl}_2, \text{Na}_2\text{SO}_4$ etc.	1-2 or 2-1	1, 2	3	$\sqrt[3]{4} \cdot C$	$\sqrt[3]{4} C f_{\pm}$	$4C^3 f_{\pm}^3$
$\text{La}(\text{NO}_3)_3, \text{K}_3\text{PO}_4$ etc.	1-3 or 3-1	1, 3	4	$\sqrt[4]{27} \cdot C$	$\sqrt[4]{27} C f_{\pm}$	$27C^4 f_{\pm}^4$ etc.

Corresponding expressions for activity and activity coefficients of electrolytes in solution when molal units are used for concentration may also be obtained in the same way. The activities will be given by,

$$a_+ = \gamma_+ m_+ \quad a_- = \gamma_- m_-$$

where γ -terms are activity coefficients and m -terms are molal concentrations.

$$\text{Similarly } a_{\pm} = (x^x y^y)^{\frac{1}{v}} m \gamma_{\pm}$$

$$\text{and } a = a_{\pm}^v = (x^x y^y) m^v (\gamma_{\pm})^v \quad \dots \text{ (XII.46)}$$

$\gamma_{\pm}$ is the mean activity coefficient. Also we have $\gamma_{\pm} = (\gamma_+^x \cdot \gamma_-^y)^{\frac{1}{v}}$

and $m_{\pm}^v = m_+^x \cdot m_-^y$, mean molality of the electrolyte in solution.

The mean activity or activity coefficients will not be the same in magnitude when molar and molal concentrations are used. The relation between $f_{\pm}$ and $\gamma_{\pm}$, and again between C and m , i.e., concentrations in two units are given by

$$\frac{\gamma}{f} = \frac{1}{\rho_0} [\rho - 0.001 CM_2] \quad \dots \text{ (XII.47)}$$

$$\text{and } \frac{m}{C} = \frac{1 + 0.001 mM_2}{\rho} \quad \dots \text{ (XII.48)}$$

where ρ = density of the solution, ρ_0 = density of pure solvent, M_2 = mol. wt. of electrolyte. To obtain the activities from molar and molal concentrations, it is necessary to determine the mean activity coefficients for various concentrations of an electrolyte. The mean activity coefficients are determined by different methods, such as from osmotic pressure, freezing point depression, solubility, *e.m.f.* measurements etc. Some of these methods are described later [see Sec. XIII.13,

XIII.18]. It must be remembered that in all such determinations, it is presumed that activity coefficient of an ion at infinite dilution is unity ; $\gamma = 1$, or $f = 1$. Therefore,

$$\begin{aligned} \text{Lt } C \rightarrow 0, \quad a_{\pm} &= f_{\pm} C_{\pm} = C_{\pm} \\ \text{and} \quad \text{Lt } m \rightarrow 0, \quad a_{\pm} &= \gamma_{\pm} m_{\pm} = m_{\pm} \end{aligned}$$

At infinite dilutions, activity and concentration of an ion are equal. In the table below are listed the mean activity coefficients (γ) of a number of electrolytes.

TABLE : MEAN IONIC ACTIVITY COEFFICIENTS (25°C)

$m \rightarrow$	0.001	0.005	0.01	0.05	0.1	0.5	1.0
HCl	0.966	0.928	0.904	0.830	0.796	0.758	0.809
KOH	—	0.92	0.90	0.82	0.80	0.73	0.76
KCl	0.965	0.927	0.901	0.815	0.769	0.65	0.606
NaBr	0.966	0.934	0.914	0.844	0.800	0.695	0.686
K ₂ SO ₄	0.89	0.78	0.71	0.52	0.43	—	—
ZnCl ₂	0.881	0.767	0.71	0.556	0.502	0.376	—
Ca(NO ₃) ₂	0.88	0.77	0.71	0.54	0.48	0.38	0.35
CuSO ₄	0.74	0.53	0.41	0.21	0.16	0.068	0.047
ZnSO ₄	0.734	0.48	0.387	0.202	0.148	0.44	0.041
MgSO ₄	—	—	0.40	0.22	0.18	0.088	0.06
La(NO ₃) ₃	—	—	0.57	0.39	0.33	—	—

A scrutiny of these results reveals that electrolytes of the same valence type, e.g., ZnCl₂ and Co(NO₃)₂, or KCl and NaBr, etc, at the same concentrations have almost equal activity coefficients, in dilute solutions. Only at higher concentrations the γ 's are individualised.

XII.17. Ionic Strength. It is necessary to define here another term namely, the ionic strength, which will have to be frequently used in our subsequent discussions. Experimental observations (see table above) show that the activity coefficient of a given strong electrolyte in very dilute solutions begins to decrease with rise in concentration, reaches a minimum and finally begins to increase with concentration. The curves shown in Fig. XII.14 illustrate this fact. It was soon realised that in very dilute solutions, the activity coefficients of electrolytes of the same type (say, uni-univalent or bi-bivalent types) are practically the same at the same ion concentration. The table bears out the truth of this statement.

Empirically the mean activity coefficient may be represented as,

$$\ln \gamma_{\pm} = -A_1 \sqrt{c}$$

where c is the concentration of the solute and it is valid in extremely low concentrations.

In a mixture, the activity coefficient of a given electrolyte depends upon the total electrolyte concentration as also on the individual characters of the different

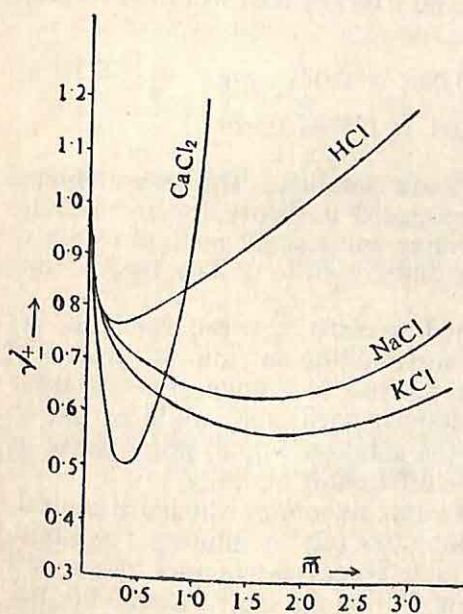


FIG. XII.14 Activity coefficients of electrolytes at various concentrations.

Resolving equation (D), the solution of ψ in terms of distance r , from the central ion is given by*

$$\psi = \frac{z\epsilon}{D} \cdot \frac{e^{-\kappa r}}{r} \quad \dots (G)$$

where $z\epsilon$ is the charge of the central ion.

$$\therefore \psi = \frac{z\epsilon}{Dr} - \frac{z\epsilon}{D} \cdot \frac{\kappa}{1+\kappa r} \approx \frac{z\epsilon}{Dr} - \frac{z\epsilon\kappa}{D} \quad \dots (H)$$

assuming κr to be quite small compared to unity.

$$\text{or} \quad \psi = \frac{z\epsilon}{Dr} - \frac{z\epsilon}{D \cdot 1/\kappa} \quad \dots (I)$$

From electrostatics, we know, the electric potential produced by the charge $z\epsilon$ of the central ion itself at a distance r from it would be given by

$$\psi_1 = \frac{z\epsilon}{Dr}$$

It may be remembered that the charge of the ionic atmosphere is equal in magnitude but opposite in sign to that of the central ion. If the charge of the ionic atmosphere be imagined to be concentrated at a point, distance $1/\kappa$, the electric potential produced by it at the ion would be $\psi_2 = -\frac{z\epsilon}{D \cdot 1/\kappa}$. The quantity $1/\kappa$

is therefore the measure of the *radius of the ionic atmosphere* and it would obviously depend upon the concentration of the solution. In equation (I) for the potential, the first term denotes the potential due to the charge of the ion itself and the second term is the potential due to the surrounding distribution of ions in the ionic atmosphere. In infinitely dilute solution κ tends to zero or the potential due to the ionic atmosphere vanishes.

Let us imagine the central ion in uncharged (or neutral) state initially and let the charge $e = z\epsilon$ be imparted to it slowly in successive amounts of infinitesimal quantities. If the potential at the surface of the ion be ψ , the work done will be given by, [using equation (H)],

$$W = \int_0^e \psi de = \int_0^e \left(\frac{e}{Da} - \frac{e\kappa}{D} \right) de$$

where 'a' is the effective radius of the ion-particle or more appropriately, the closest approach between the ions. The work of charging the ion in infinite dilution and in a solution of a given concentration would be different. The work involved in the two cases are :

$$\begin{aligned} (i) \text{ In infinite dilution : } W_1 &= \int_0^{z\epsilon} \left(\frac{e}{Da} - \frac{e\kappa}{D} \right) de = \int_0^{z\epsilon} \frac{e}{Da} de \\ (\text{since } \kappa &= 0) &= \frac{z^2\epsilon^2}{2Da} \end{aligned}$$

*Transformation into polar coordinate gives

$$\nabla^2 \psi = \kappa^2 \psi$$

or

$$\frac{1}{r^2} \left[\frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) \right] - \kappa^2 \psi = 0$$

Putting $\psi = \frac{v}{r}$, $\frac{d^2 v}{dr^2} - \kappa^2 v = 0$, from which solution (G) is obtained.

$$(ii) \text{ In a given solution, } W_2 = \int_0^{z\epsilon} \left(\frac{e}{Da} - \frac{e\kappa}{D} \right) de$$

$$= \frac{z^2\epsilon^2}{2Da} - \frac{z^2\epsilon^2}{2D} \cdot \kappa$$

Hence, the work done in transferring the charged ion from the solution in infinite dilution to that in given concentration,

$$\Delta W = W_2 - W_1 = -\frac{z^2\epsilon^2}{2D} \kappa \quad \dots (J)$$

If the solutions were ideal and if there were no electrical interionic forces, then the change in Gibbs potential in the transfer of the ion from a very dilute solution (concentration m_0 molal) to a given solution (concentration m molal) would be

$$\Delta G = \frac{RT}{N} \ln \frac{m}{m_0}, \text{ where } N \text{ is Avogadro number.}$$

In real solutions, the interionic forces are to be taken into account and the Gibbs potential change would be,

$$\Delta G = \frac{RT}{N} \ln \frac{m}{m_0} + \Delta W = \frac{RT}{N} \ln \frac{m}{m_0} - \frac{z^2\epsilon^2}{2D} \kappa \quad \dots (K)$$

Again for real solutions, introducing activity terms, we have

$$\Delta G = \frac{RT}{N} \cdot \ln \frac{a}{a_0} = \frac{RT}{N} \ln \frac{m\gamma}{m_0\gamma_0} = \frac{RT}{N} \ln \frac{m\gamma}{m_0}$$

(γ -terms are activity coefficients and in very dilute solutions $\gamma_0 \rightarrow 1$)

$$\text{or} \quad \Delta G = \frac{RT}{N} \ln \frac{m}{m_0} + \frac{RT}{N} \ln \gamma \quad \dots (L)$$

$$\text{Comparing equation (K) and (L), } \frac{RT}{N} \ln \gamma = -\frac{z^2\epsilon^2}{2D} \cdot \kappa$$

$$\text{or} \quad \ln \gamma = -\frac{z^2\epsilon^2 N}{2DRT} \cdot \kappa \quad \dots (M)$$

In equation (F) it is seen, $\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum n_i z_i^2$ in which n_i is the number of the i -th species of ion per c.c.

$$\text{The molar concentration of the ion, } c_i = \frac{n_i}{N} \cdot 1000$$

$$\therefore \text{ The molal concentration of the ion, } m_i = \frac{n_i}{N} \cdot \frac{1000}{d}$$

where d is the density of the solution, the same as that of the solvent when the solution is dilute.

$$\therefore \quad n_i = \frac{Nd}{1000} \cdot m_i$$

$$\text{or} \quad \sum n_i z_i^2 = \frac{Nd}{1000} \sum m_i z_i^2$$

$$\begin{aligned}
 \text{Rewriting equation (M), } \ln \gamma &= -\frac{z^2 \epsilon^2 N}{2DRT} \cdot \kappa \\
 &= -\frac{z^2 \epsilon^2 N}{2DRT} \left(\frac{4\pi \epsilon^2}{DkT} \cdot \frac{Nd}{1000} \sum m_i z_i^2 \right)^{\frac{1}{2}} \\
 &= -\frac{z^2 \epsilon^2 N}{2DRT} \left(\frac{4\pi \epsilon^2}{DkT} \cdot \frac{Nd}{1000} \right)^{\frac{1}{2}} \sqrt{\sum m_i z_i^2}
 \end{aligned}$$

Since ionic strength (Sec. XII.17) is given by, $i = \frac{1}{2} \sum m_i z_i^2$

$$\begin{aligned}
 \text{We have, } \ln \gamma &= -z^2 \left(\frac{\epsilon^2 N}{2DRT} \cdot \sqrt{\frac{4\pi \epsilon^2 Nd}{DkT \cdot 1000}} \right) \sqrt{2i} \\
 &= -Bz^2 \sqrt{i} \quad \dots (N)
 \end{aligned}$$

$$\begin{aligned}
 \text{where } B &= \sqrt{2} \left(\frac{\epsilon^2 N}{2DRT} \cdot \sqrt{\frac{4\pi \epsilon^2 Nd}{DkT \cdot 1000}} \right) \\
 &= \frac{1}{(DT)^{3/2}} \cdot \left(\frac{\epsilon^2 N}{R} \cdot \sqrt{\frac{2\pi \epsilon^2 Nd}{k \cdot 1000}} \right) \quad \dots (O)
 \end{aligned}$$

and is a constant when D and T are unaltered.

The equation (N) is then an expression for the activity coefficient γ , in terms of known measurable data.

The mean activity coefficient $\gamma_{\pm}$ of an electrolyte, say $A_{v+}B_{v-}$ is given by

$$\gamma_{\pm}^{v_+ + v_-} = \gamma_+^{v_+} \cdot \gamma_-^{v_-}$$

$$\begin{aligned}
 \text{or } \ln \gamma_{\pm} &= \frac{v_+ \ln \gamma_+ + v_- \ln \gamma_-}{v_+ + v_-} \\
 &= \frac{v_+ (-Bz_+^2 \sqrt{i}) + v_- (-Bz_-^2 \sqrt{i})}{v_+ + v_-} \\
 &= -B\sqrt{i} \left[\frac{v_+ z_+^2 + v_- z_-^2}{v_+ + v_-} \right]^* \\
 &= -B\sqrt{i} \cdot z_+ \cdot z_- \\
 \therefore \log_{10} \gamma_{\pm} &= -\frac{B}{2.303} |z_+| \cdot |z_-| \cdot \sqrt{i} = -Az_+ z_- \sqrt{i} \quad \dots (P)
 \end{aligned}$$

where z_+ and z_- are the numerical values of the valence of the two ions of the electrolyte and $A = B/2.303$.

Using the values $\epsilon = 4.77 \times 10^{-10}$ e.s.u. ; $N = 6.06 \times 10^{23}$; $k = 1.36 \times 10^{-16}$ ergs. at 25°C , in aqueous solutions, where $D = 78.54$, the value of A comes out to be 0.509.

$$\therefore \log_{10} \gamma_{\pm} = -0.509 z_+ z_- \sqrt{i} \approx -0.5 z_+ z_- \sqrt{i} \quad \dots (Q)$$

So, for different types of electrolytes, the mean activity coefficient would be,

	$\log_{10} \gamma_{\pm}$
Uni-univalent	$-0.5\sqrt{i}$
Uni-bivalent	$-1.0\sqrt{i}$
Uni-trivalent	$-1.5\sqrt{i}$
Bi-Bivalent	$-2.0\sqrt{i}$ etc.

* $v_+ z_+^2 + v_- z_-^2$
 $= v_- z_- z_+ + v_+ z_+ z_-$
 $= z_+ z_- (v_+ + v_-)$

For a single uni-univalent electrolyte in aqueous solution of molality m at 25°C ,

$$\log_{10}\gamma_{\pm} = -0.5\sqrt{i} = -0.5\sqrt{m}$$

The equation (Q) is often mentioned as the *Debye-Hückel Limiting Law* and it gives the method of calculation of the activity coefficient of an electrolyte theoretically, at very dilute solutions. The law will be strictly valid as the concentration approaches zero, i.e., at infinite dilution. The validity of the Debye-Hückel theory for very dilute solutions ($i < 0.01$) has been tested in two ways.

I. Since $\log \gamma_{\pm} = -Az_+z_-\sqrt{i}$, the plot of $-\log \gamma_{\pm}$ against $\sqrt{i}$ in dilute solutions would be linear and the slope of the line would give the value of Az_+z_- . This has been experimentally established. The activity coefficients of different cobaltamine salts were determined from solubility measurements in different ionic strengths (Brönsted and Lamer); the ionic strengths were varied by addition of salts, like NaCl, KNO_3 , BaCl_2 etc. The linear graphs obtained on plotting $\sqrt{i}$ vs $-\log \gamma_{\pm}$ are shown in Fig. (XII.15). The slopes obtained from the graphs corresponded to the calculated values of Az_+z_- . Moreover the same linearity was obtained irrespective of the nature of the salt added to vary the ionic strength, as expected from the theory.

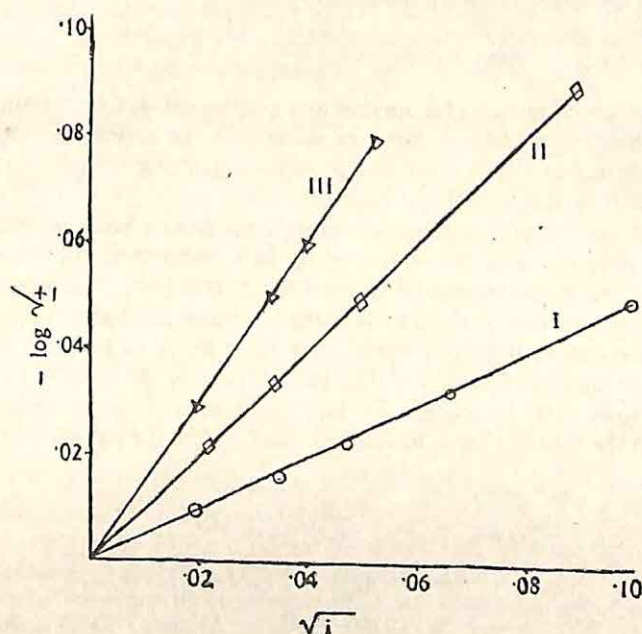


FIG. XII.15 Activity coefficients vs. ionic strength.
1. Uni-univalent. II. Uni-bivalent. III. Uni-trivalent.

II. It will be seen from equation (O) that for a given electrolyte the value of 'A' should be proportional to $\frac{1}{(DT)^{3/2}}$. Varying the temperature, the dielectric

constant was widely altered. The slope of the line $\log \gamma_{\pm}$ vs $\sqrt{i}$ at different temperatures has been determined to calculate A. The experimental results satisfy the theoretical requirements.

Apart from the fact that the limiting law enables us to calculate $\gamma_{\pm}$ in dilute solutions, where experimental values may not be available, the law is also used for various other purposes. Some of its applications will be seen in subsequent sections.

XII.19. The Debye-Hückel Theory in Concentrated Solution. It has been mentioned earlier that the Debye-Hückel theory would be valid only in very dilute solutions. In solutions of appreciable concentration, the extension of the limiting law has been made chiefly by Hückel and by Brönsted.

In deriving the Debye-Hückel equation two approximations have been made which are not permissible in more concentrated solutions. (i) The potential due to the ionic atmosphere ψ_2 has

been approximated to $\frac{-ze\kappa}{D}$ assuming κr to be very small, which is not so in case of concentrated solutions (see equation (H) Sec. XII.18). (ii) The dielectric constant D of the medium has been assumed to be constant throughout the medium, which is not strictly true. In order to apply the Debye-Hückel equation to solutions of appreciable concentration, corrections have to be introduced on these two counts.

(i) The potential due to the ionic atmosphere should be

$$\psi_a = -\frac{ze}{D} \cdot \frac{\kappa}{1+\kappa r}$$

Using this expression for the ionic atmosphere and following the same treatment as before, it can be shown,

$$\log_{10} \gamma_{\pm} = -\frac{Az_+z_-\sqrt{i}}{1+a\kappa}$$

The value of κ is

$$\left(\frac{4\pi e^2}{DkT} \cdot \frac{Nd}{1000} \right)^{\frac{1}{2}} \sqrt{2i} = A_1 \sqrt{i}$$

where A_1 stands for the quantity within the paranthesis.

Hence

$$\log_{10} \gamma_{\pm} = -\frac{Az_+z_-\sqrt{i}}{1+aA_1\sqrt{i}} \quad \dots (R)$$

This expression would always give smaller and smaller values for $\gamma_{\pm}$ with increasing concentrations. Experimental measurements however show that the activity coefficients first decrease with rise in the concentration and then increase after passing through a minimum value (Fig. XII.14). The expression, therefore, needs further correction.

(ii) The solvent molecules themselves are permanent dipoles and are influenced by the ions. The electric forces near the ions are quite strong. In consequence, the solvent molecules may compete with other ions in the formation of the ionic atmosphere. The orientation of the polar solvent molecules in the vicinity of the ions is likely to reduce the dielectric constant (D) appreciably. The dielectric constant therefore would vary from point to point. It has been presumed that this dielectric constant is a function of the concentration or the ionic strength. A complicated set of calculation shows that, to account for this variation of dielectric constant, an additional term proportional to the ionic strength has to be introduced in the equation (R), such that we can write,

$$\log_{10} \gamma_{\pm} = -\frac{Az_+z_-\sqrt{i}}{1+aA_1\sqrt{i}} + A_2i \quad \dots (S)$$

or

$$\begin{aligned} \log_{10} \gamma_{\pm} &= -Az_+z_-\sqrt{i} + aA_1z_+z_-\sqrt{i} + A_2i \\ &= -Az_+z_-\sqrt{i} + Ci \end{aligned}$$

C = a constant for a given electrolyte.

This expression is in fair agreement with experimental results and is an extension of the Debye-Hückel Law for the concentrated solutions.

References for further study

1. Introduction to Electrochemistry—Glasstone
2. The conductivity of solutions—Davies
3. Principles and applications of Electrochemistry—Creighton and Koehler
4. The principles of Electrochemistry—MacInnes
5. The physical chemistry of Electrolytic solutions—Harned and Owen
6. Solution of Electrolytes—Hammett

Problems

1. A steady current passed through a solution of AgNO_3 deposits 0.5000 gms of silver in 1 hr. Calculate the number of coulombs. What volume of hydrogen at 27°C and 750 mm pressure would the same current liberate in 1 hr?
2. Calculate the quantity of electricity which would be required to reduce 10.25 gms of nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) to aniline ($\text{C}_6\text{H}_5\text{NH}_2$). If the voltage across the electrodes in the electrolytic cell be 2.4 volts, how much energy in calories is consumed in the process of reduction.

3. A solution of HCl was electrolysed in a transport tube with Pt electrodes. The amount of HCl in the cathode compartment before and after electrolysis are 0.1820 gms and 0.1670 gms respectively. The silver deposited in a silver coulometer in the same circuit was 0.2520 gms. What is the transport number of Cl^- ?

4. In a Hittorf tube with silver electrodes a 0.1N AgNO_3 solution was electrolysed. At the end of electrolysis, 20.10 gm of solution in the anode compartment was found to contain 39.66 mg of silver, and 27.10 gm of solution in the cathode compartment contained 11.14 mg of silver. The silver coulometer in series gave a deposit of 32.10 mg of silver. Show that the transport number of silver ion would be 0.44.

5. In a moving boundary experiment with a 0.02N NaCl solution a current of 0.0016 ampere moved the boundary through a distance 6.00 cms in 2070 sec. The cross-section of the tube is 0.1115 cm^2 . Calculate the transport number of both ions.

6. The specific conductance of 0.01N KCl solution at 18°C is 0.001225. In a given conductivity cell at 18°C , the resistance of 0.01N KCl solution was found to be 145.00 ohms and that of 0.002N K_2SO_4 was 712 ohms. What is the cell-constant? What is the equivalent conductance of 0.002N K_2SO_4 ?

7. The equivalent conductances of NaCl, HCl and sodium monochloroacetate at 25°C at infinite dilutions are 127, 426 and $89.8 \text{ ohm}^{-1} \text{ cm}^2$. What is λ_0 for monochloroacetic acid at 25°C ?

8. The equivalent conductance of an infinitely dilute solution of NH_4Cl is 150 and the ion conductances of OH^- and Cl^- ions are 198 and 76 respectively. What will be the value of λ_0 for NH_4OH ? If the equivalent conductances of a 0.01N solution of NH_4OH be 9.6, what will be its degree of dissociation?

9. The resistance of a conductivity cell filled with 0.02N KCl at 18°C is 17.6 ohms; filled with 0.1N acetic acid the resistance is 92 ohms. The sp. conductance of 0.02N KCl at 18°C is $0.0024 \text{ ohm}^{-1} \text{ cm}^{-1}$. At 18°C , $I_{H^+} = 315$, $I_{Ac^-} = 35$. Show that the 0.1N acetic acid is dissociated to an extent of 13.2% at 18°C .

10. At 25°C , the eqv. conductance of NaI solutions are as follows,

Conc.	5×10^{-4}	10×10^{-4}	50×10^{-4}
λ	125.36	124.25	121.25

Calculate the ion conductance of iodide ion if that of sodium ion be 50.1.

11. At 25°C , the mobility at infinite dilution of NH_4^+ ion is 76×10^{-5} and that of acetate ion $42 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$. Calculate λ_0 for ammonium acetate and the transport number of the two ions.

12. At 25°C , for a 0.02 molar AgNO_3 solution, $\lambda = 128.8$ and $t_{Ag^+} = 0.477$. Find out the mobilities of Ag^+ and NO_3^- ions in the same solution.

13. For KCl in aqueous solution $\lambda_0 = 149.8$. What will be the equivalent conductance λ of a (1×10^{-3}) molar KCl solution assuming Onsager equation? (See eqn. XII.31).

14. What is the ionisation constant of chloroacetic acid, if the equivalent conductance of its 0.014N solution be 109 at 25°C . Given $I_{H^+} = 349.8$ and $I_{Ac^-} = 40.0$.

15. Calculate the ionic strengths of 0.1 M solution of KClO_4 , Na_2SO_4 , $\text{K}_4\text{Fe}(\text{CN})_6$ and CuSO_4 .

16. Use Debye-Hückel limiting law to calculate the mean ionic activity coefficient of a 1×10^{-3} molal aqueous solution of (a) Na_2SO_4 (b) $\text{K}_3\text{Fe}(\text{CN})_6$.

17. The Arrhenius dissociation constant of propionic acid at 25°C is 1.35×10^{-5} . Calculate the (a) degree of dissociation (b) H^+ -ion concentration in a 0.005 molar solution.

What will be thermodynamic dissociation constant if the degree of dissociation is accepted as correct and Debye-Hückel Law is applied?

18. At 35°C , the conductivity of a saturated solution of silver chloride was found to be 4.40×10^{-6} and that of water 1.2×10^{-6} . Calculate the solubility of silver chloride at the temperature. (The table may be consulted for ion conductances).

19. The specific conductance of thallous bromide is 2.16×10^{-4} and that of water 0.044×10^{-6} . The equivalent conductance at infinite dilution is 138.2. Find out the solubility of thallous bromide in gms per litre at the same temperature.

20. The freezing point of 0.025 molal copper sulphate is -0.061°C . The equivalent conductance of this solution at 18°C is 51. Calculate the degree of ionisation of CuSO_4 in solution both from freezing point and from conductance. (Standard data may be taken from the relevant tables.)

ELECTROMOTIVE FORCE : IONIC EQUILIBRIA

XIII.1. Galvanic Cells. A galvanic cell is a device in which the free energy of a chemical process is converted into electrical energy. Usually such a cell consists of two electrodes immersed in one or more suitable electrolytes. When the electrodes are connected externally by a metallic conductor, current flows from one electrode to another and inside the cell chemical changes occur at the surface of the electrodes. A galvanic cell is thus rightly called an *electrochemical cell*, whereas an *electrolytic cell* is one in which electrical energy from an external source is used to carry out a chemical change. To illustrate a typical galvanic cell, we may cite the old and familiar Daniell cell commonly used in the laboratory.

In a Daniell cell a zinc rod is immersed in a ZnSO_4 solution and a copper rod in a CuSO_4 solution. The two solutions are kept separated by a porous barrier. The barrier allows current to pass through but prevents mass diffusion. Zinc and copper rods are the two electrodes. When these are connected externally by a metallic wire, current flows from copper to zinc through the wire. Copper is said to be the positive pole and zinc the negative. (Fig. XIII.1).

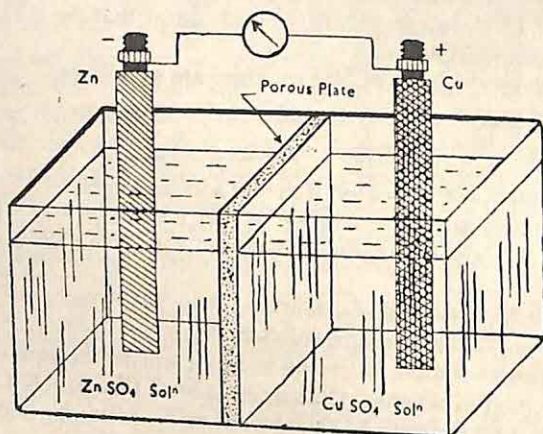
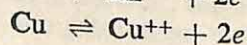


FIG. XIII.1 A Galvanic cell (Daniell cell)

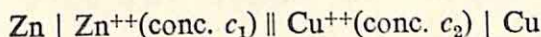
In this cell both the electrodes zinc and copper are surrounded by their own ions in solution. There exists an equilibrium between the atoms in the electrode and the ions in solution at each electrode, as



But zinc has a greater tendency to ionise than copper and so zinc atom goes into solution leaving behind two electrons in the metal electrode. On the other hand, at the copper electrode copper ions from the solution are deposited by accepting two electrons each from the electrode. So there is an excess of electrons at the zinc electrode and dearth of the same at the copper electrode. When the circuit is closed electrons flow from zinc to copper through the wire to feed the copper ions in the process of discharge of copper. This is how the electrical energy (or current) is produced which may be used for the purpose of external work.

It is obvious the zinc electrode, where zinc gives up its electrons *i.e.*, oxidation occurs, is the anode or negative electrode. The copper electrode, where copper ions

take up electrons *i.e.*, reduction occurs, is the cathode or positive electrode. The galvanic cell is represented as



where vertical lines indicate phase boundaries.

The cell reaction is $\text{Zn} + \text{Cu}^{++} = \text{Zn}^{++} + \text{Cu}$

It is the usual custom to write the anode of the cell on the left and the cathode to the right in representing a cell. It is also our common convention that the current in the external circuit is considered to flow from cathode to anode (Cu to Zn) although the electrons are flowing through the wire in the opposite direction (from zinc to copper).

The flow of current and the chemical changes at the electrode continue as long as the circuit is closed. The chemical action ceases when the circuit is left open and there would be no flow of current.

Many other electrochemical cells are in use. A few of these are mentioned here.

Cell	Chemical reaction
(i) $\bar{\text{Zn}} \mid \text{Zn}^{++}(\text{soln}) \mid \text{Hg}_2^{++}(\text{soln}) \mid \overset{+}{\text{Hg}}$	$\text{Zn} + \text{Hg}_2^{++} = \text{Zn}^{++} + 2\text{Hg}$
(ii) $\bar{\text{Pb}} \mid \text{H}_2\text{SO}_4 \mid \text{PbO}_2(\overset{+}{\text{Pb}})$	$\text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 = 2\text{PbSO}_4 + 2\text{H}_2\text{O}$
(iii) $\bar{\text{Cd}}(\text{Hg}) \mid \text{CdSO}_4, 8/3\text{H}_2\text{O} \mid \text{Hg}_2\text{SO}_4 \mid \overset{+}{\text{Hg}}$ (amalgam) (satd.) (satd.)	$\text{Cd} + \text{Hg}_2\text{SO}_4 = \text{CdSO}_4 + 2\text{Hg}$

Reversible and Irreversible Cells. The electrochemical cells may be *reversible* or *irreversible*. In a reversible cell it is implied that the chemical reaction occurring in the cell may proceed in either direction depending upon the direction of flow of the current. When the circuit of the cell is closed, a reaction occurs in the cell and we obtain a current. Thereafter if we apply a driving force (e.m.f.) from an external source so as to cause a current to flow in the opposite direction, the chemical action is reversed. The driving and opposing forces may be only infinitesimally different. When these requirements are satisfied the cell is reversible. When the chemical reaction cannot be reversed by the application of external e.m.f. the cell is irreversible.

The Daniell cell discussed earlier is an example of a reversible cell. When 2 coulombs of electricity are produced, 65/96500 gm of zinc goes into solution at the anode and 63.5/96500 gm of copper is deposited at the cathode. If now an external e.m.f. is applied such that 2 coulombs of electricity are passed in the opposite direction, the cell will return to its original state, *i.e.*, the quantity of zinc as dissolved earlier will be deposited at the anode and the previous quantity of copper will be dissolved at the cathode. The cell is thus reversible.

On the other hand if we consider the cell



in which 1 faraday of electricity is produced, when 1 gm-equivalent zinc goes into solution and one gm-equivalent hydrogen is liberated at the cathode (Cu). If now 1 faraday of electricity is passed through the cell in the opposite direction 1 gm-equivalent of copper goes into solution and 1 gm-equivalent of hydrogen is liberated at the zinc-electrode. The original state is not reproduced; the reaction is also not reversed. This is an irreversible cell.

In a cell there are two electrodes. Each of the electrodes in contact with its ions is called a *single electrode* or *half-cell*. In a reversible cell each half-cell is also reversible. Thus, in Daniell cell the anode zinc ($\text{Zn} \mid \text{Zn}^{++}$) in contact with zinc ions is a reversible half-cell; and also copper ($\text{Cu} \mid \text{Cu}^{++}$) in contact with copper ions is the other reversible half-cell.

To deal with the energy relations of cells, thermodynamic principles are extensively employed. The thermodynamic relations are applicable only to reversible systems. That is why the reversibility of cells is of utmost importance.

XIII.2. Measurement of EMF of Cells. The e.m.f. of a cell is measured with the help of a potentiometer. The principle involved can be easily understood from Fig. XIII.2. AB is the potentiometer slide wire of uniform cross-section and having high resistance. A storage cell C is connected across the terminals of the slide wire AB , such that potential drops from A to B . Now the cell X , whose e.m.f. is required, is connected to A , such that its e.m.f. opposes that of C . (That is, A is connected to positive terminals of both X and C .) The other terminal of cell X is connected through a galvanometer (G) to a sliding contact P . This is moved along the slide wire until there is no deflection in the galvanometer. This means that the e.m.f. of the cell X just balances the drop of potential between A and P .

FIG. XIII.2 Measurement of EMF of a cell.

Next a standard cell (S) is taken to replace the cell X and the experiment is repeated. The e.m.f. of the cell S now opposes that of C in the slide wire. Let the contact point now be Q when there would not be any deflection in the galvanometer. That means the drop of potential in the slide wire from A to Q just balances the e.m.f. of the standard cell.

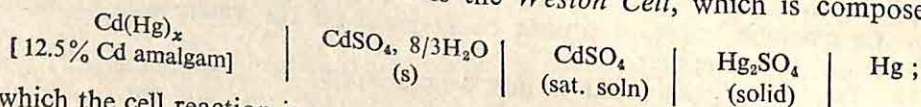
If E_x and E_s be the e.m.f.'s of the given cell and the standard cell, then

$$\frac{E_x}{E_s} = \frac{\text{Drop of potential from } A \text{ to } P}{\text{Drop of potential from } A \text{ to } Q} = \frac{\text{Resistance of } AP}{\text{Resistance of } AQ} = \frac{\text{length } AP}{\text{length } AQ}$$

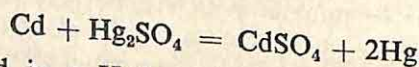
since the wire is of uniform cross section. The two lengths being known and since E_s , the e.m.f. of the standard cell is known, E_x is easily determined.

Though measurements are made with closed circuits, but when the e.m.f. of the cell is balanced, no current practically passes. As such the potential E_x measured is really the e.m.f. of X with the circuit open.

The most widely used standard is the *Weston Cell*, which is composed as



in which the cell reaction is



The cell is prepared in a H-shaped vessel—one arm containing the electrode 12.5% Cd-amalgam and the other arm containing mercury in contact with a paste of Hg and mercurous sulphate. The whole of the vessel is then filled up with saturated solution of CdSO_4 . Some crystals of $3\text{CdSO}_4, 8\text{H}_2\text{O}$ being added over the negative electrode. The vessel is then sealed. The electrodes are connected to the external circuit through two Pt-wires sealed at the bottom of the two electrodes (Fig. XIII.3).

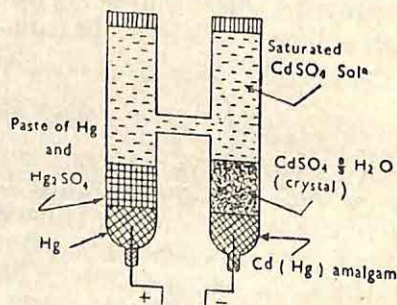


FIG. XIII.3 A standard cell (Weston Cell)

Its emf is measured by comparison with p.d. across a standard known resistance carrying an absolutely known current (say, Ag-coulometer).

The e.m.f. of Weston cell remains constant for a long period and has a high reproducibility. Its temperature coefficient is also quite small. At 20°C,

$$E = 1.01845 \text{ volts and } \frac{dE}{dT} = -0.00004 \text{ volts degree}^{-1}$$

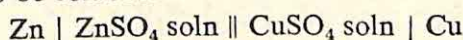
XIII.3. EMF of a Cell and Free Energy Change. The chemical process occurring in any galvanic cell is exothermic and if the process be carried out in a beaker a quantity of heat will be evolved. The same change when processed through the voltaic cell yields energy in the electrical form. It was formerly presumed that the electrical energy obtained from a cell is quantitatively equivalent to the heat of reaction of the chemical change occurring there in. That is,

$$(\text{heat of reaction}), \Delta H = -n\mathcal{F}E, (\text{electrical energy}),$$

$$\text{or} \quad E = \frac{-\Delta H}{n\mathcal{F}} \quad \dots (\text{XIII.1})$$

where $n\mathcal{F}$ is the charge associated with the transfer of a gm-mole of substance deposited or liberated; $\mathcal{F}$ is Faraday and E = e.m.f. of the cell.

This appeared to be corroborated from studies with Daniell cell,



The reaction in the cell may be represented as follows :



The e.m.f. of the cell is 1.09 volts, and the quantity of charge carried, when 1 gm-mole of zinc dissolves, is $2\mathcal{F}$ ($\mathcal{F} = 96500$ coulombs).

Hence, the electric energy output,

$$\begin{aligned} n\mathcal{F}E &= 2 \times 96500 \times 1.09 \text{ volt-coulombs} \\ &= \frac{2 \times 96500 \times 1.09}{4.2} \text{ calories} = 50010 \text{ calories.} \end{aligned}$$

This is almost the same as the heat of the reaction, 50300 calories. Hence equation (XIII.1) seemed correct.

It was Helmholtz who pointed out the fortuitous concordance of the two values in the case of the Daniell cell. Really, the output of the electrical energy should correspond to the net available work of the process and not to the heat of reaction. This means that the electrical energy, $n\mathcal{F}E$, should be equivalent to the drop in Gibbs potential ($-\Delta G$).

$$\text{Hence,} \quad -\Delta G = n\mathcal{F}E. \quad \dots (\text{XIII.2})$$

From the Gibbs-Helmholtz equation, we know

$$\Delta G = \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_P$$

The voltaic-cell processes are isochoric and isobaric. Hence in such cases, ΔG and ΔF are equal. When the cell yields the electric energy, there is a drop of free energy. Since $\Delta F = \Delta G = -n\mathcal{F}E$, we have,

$$-n\mathcal{F}E = \Delta H + T \left[\frac{\partial(-n\mathcal{F}E)}{\partial T} \right] \quad \dots (\text{XIII.3})$$

$$\text{i.e.,} \quad E = -\frac{\Delta H}{n\mathcal{F}} + T \left(\frac{\partial E}{\partial T} \right)_P \quad \dots (\text{XIII.4})$$

This relation is universally employed for the e.m.f. of a cell. The second term on the right-hand side which involves the temperature coefficient is an addition to the previous relation (XIII.1). In the Daniell cell it has been found that $\frac{\partial E}{\partial T}$ is almost zero. That is why the previous relation seemed satisfactory in that case.

To illustrate ; let us take the Clarke cell, in which

$$E = 1.420 \text{ and } \frac{\partial E}{\partial T} = -1.2 \times 10^{-3}, \text{ at } 25^\circ\text{C.}$$

The cell : $\text{Zn} \mid \text{ZnSO}_4 \text{ soln} \parallel \text{Hg}_2\text{SO}_4 \mid \text{Hg}$

Cell reaction : $\text{Zn} + \text{Hg}_2\text{SO}_4 = \text{ZnSO}_4 + 2\text{Hg}$; (heat of reaction $\Delta H = -81200$ cal)

If we assume $\Delta H = -n\mathcal{F}E$

$$\text{then, } \Delta H = -\frac{2 \times 96500 \times 1.420}{4.2} = -65250 \text{ calories}$$

This differs considerably from the observed heat of reaction of the process. Now if we use the Gibbs-Helmholtz relation, then

$$\begin{aligned} \Delta H &= -n\mathcal{F}E + n\mathcal{F}T \cdot \frac{\partial E}{\partial T} \\ &= -\frac{2 \times 96500 \times 1.420}{4.2} + \frac{2 \times 96500}{4.2} \times (273 + 25) \times (-1.2 \times 10^{-3}) \\ &= -81690 \text{ calories.} \end{aligned}$$

Obviously, the relation (XIII.4) is the appropriate one.

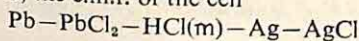
Further, from equation (IV.65) we know $\Delta S = -\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$

$$\text{or } \Delta S = -\left[\frac{\partial(-n\mathcal{F}E)}{\partial T}\right]_P = n\mathcal{F} \frac{\partial E}{\partial T} \quad \dots \text{(XIII.5)}$$

that is, we can calculate the entropy-change from the temperature coefficient of the e.m.f. of the cell.

Thus, knowledge of e.m.f. of a cell enables us to find out ΔS , ΔG and also ΔH of the chemical process in the cell, for $\Delta H = -\Delta G + T\Delta S$.

Problem. At 25°C , the e.m.f. of the cell



is 0.49 volts and its temperature coefficient $\frac{\partial E}{\partial T} = -1.8 \times 10^{-4}$ volt/degree. Calculate (a) the entropy-change when 1 gm-mol of silver is deposited and (b) the heat of formation of silver-chloride, if the heat of formation of lead chloride is $H_{\text{PbCl}_2} = -86000$ cal.

The cell reaction : $\frac{1}{2}\text{Pb} + \text{AgCl} = \text{Ag} + \frac{1}{2}\text{PbCl}_2$

$$\Delta G = -n\mathcal{F}E = -\frac{1 \times 96500}{4.2} \times 0.49 = -11260 \text{ cal}$$

$$\text{And } \Delta S = -\frac{\partial(\Delta G)}{\partial T} = n\mathcal{F} \frac{\partial E}{\partial T} = \frac{96500}{4.2} (-1.8 \times 10^{-4}) = -4.14 \text{ cal/degree.}$$

The heat of reaction of the chemical change,

$$\begin{aligned} \Delta H &= -\Delta G + T\Delta S = -11260 + 298 \times (-4.14) \text{ cal.} \\ &= -12494 \text{ cal.} \end{aligned}$$

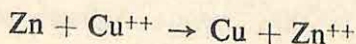
This heat of reaction is the algebraic sum of the heats of formation of the components ;

$$\begin{aligned} \Delta H &= H_{\text{Ag}} + \frac{1}{2}H_{\text{PbCl}_2} - \frac{1}{2}H_{\text{Pb}} - H_{\text{AgCl}} \\ &= 0 - \frac{1}{2} \times 86000 - \frac{1}{2} \times 0 - H_{\text{AgCl}} \end{aligned}$$

or heat of formation of silver chloride,

$$H_{\text{AgCl}} = -\frac{1}{2} \times 86000 - \Delta H = -30506 \text{ calories/mole.}$$

Thus far, the output of electrical energy from a cell has been proposed to be equal to the free energy change and the same has been corroborated from experimental results. The relation $\Delta F = -n\mathcal{F}E$ can also be thermodynamically established if we proceed in the following way. In the Daniell cell, the chemical process is



Now, assuming ions, molecules etc., as separate entities, let us denote their chemical potentials as,

- μ_1 = Chemical potential of Zn^{++} ions in the metal
- μ_2 = Chemical potential of Zn^{++} ions in the solution
- μ_3 = Chemical potential of Cu^{++} ions in the metal
- μ_4 = Chemical potential of Cu^{++} ions in the solution
- μ_5 = Chemical potential of Zn atoms in the metal
- μ_6 = Chemical potential of Cu atoms in the metal
- μ_7 = Chemical potential of electrons in the Zn-metal
- μ_8 = Chemical potential of electrons in the Cu-metal.

Remembering that, at equilibrium, the chemical potential of any entity must be the same in every phase, we have

$$\text{since, } \mu_1 = \mu_2 \text{ and } \mu_3 = \mu_4$$

$$\text{Zn} \rightleftharpoons \text{Zn}^{++} + 2e; \quad \text{Cu} \rightleftharpoons \text{Cu}^{++} + 2e$$

Remembering the chemical potential of reactants and resultants at equilibrium as equal, we have

$$\mu_5 = \mu_1 + 2\mu_7 = \mu_2 + 2\mu_7$$

$$\mu_6 = \mu_3 + 2\mu_8 = \mu_4 + 2\mu_8$$

Subtracting, $\mu_5 - \mu_6 = \mu_2 - \mu_4 + 2(\mu_7 - \mu_8)$

or, rewriting $(\mu_6 + \mu_2) - (\mu_5 + \mu_4) = -2(\mu_7 - \mu_8)$

That is, when the chemical change occurs,

$$(\mu_{\text{Cu}} + \mu_{\text{Zn}^{++}}) - (\mu_{\text{Zn}} + \mu_{\text{Cu}^{++}}) = -2(\mu_e^{\text{Zn}} - \mu_e^{\text{Cu}})$$

$$\text{or } \Sigma\mu = -2(\mu_e^{\text{Zn}} - \mu_e^{\text{Cu}})$$

$$\text{where } \Sigma\mu = \mu_{\text{resultants}} - \mu_{\text{reactants}}$$

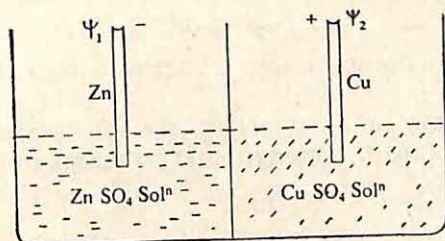


FIG. XIII.4 Daniell cell

Let ψ_1 and ψ_2 be the electric potentials at the zinc and copper terminals above the solution. Then e.m.f. of the cell E is given by

$$E = \psi_2 - \psi_1$$

(since conventionally copper end is the positive terminal wherefrom current flows in the external circuit).

The chemical potentials of an electron (charge $-\epsilon$) at the two terminals of electric potentials ψ_1 and ψ_2 would then be,

$$\mu_e^{\text{Zn}} = \mu_e^0 - \psi_1\epsilon; \quad \mu_e^{\text{Cu}} = \mu_e^0 - \psi_2\epsilon$$

where μ_e^0 is the chemical potential at the standard state.

$$\text{Then, } \mu_e^{\text{Zn}} - \mu_e^{\text{Cu}} = -\epsilon[\psi_1 - \psi_2]$$

$$\text{Therefore, } \Sigma\mu = -2[\mu_e^{\text{Zn}} - \mu_e^{\text{Cu}}] = +2\epsilon[\psi_1 - \psi_2] = -2\epsilon E$$

The factor 2, indicating the number of electrons transferred, may be replaced by 'n' in a general process.

So that

$$\Sigma\mu = -n\epsilon E$$

In the transformation of a *gm-mole* of the substance in the cell, we may write,

$$\Sigma \mu = -n\mathcal{F}E$$

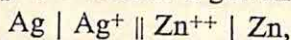
Using Gibbs'-Duhem relation, $\Sigma \mu = \Delta G = \Delta F$

$\therefore$

$$\Delta G = -n\mathcal{F}E$$

The equation (XIII.2) is thus a thermodynamic requirement.

It is known that when a reaction occurs spontaneously ΔG (or ΔF) is negative and hence e.m.f. is positive (equation XIII.2). If we find in a galvanic arrangement e.m.f. is negative, then ΔG will be positive; the reaction is not likely to occur spontaneously. For example, if we have a galvanic cell arranged as

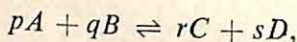


the e.m.f. is negative ($E = -1.6$ volts). It can be immediately concluded that Ag will not dissolve to deposit zinc. The opposite arrangement will have positive e.m.f. and hence negative ΔG . That is, zinc will spontaneously dissolve to deposit Ag.

The spontaneity of a reaction can be judged from the sign of the e.m.f. of the cell. The criteria are

ΔG	E	Cell reaction
—	+	spontaneous
0	0	equilibrium
+	—	non-spontaneous

XIII.4. EMF and Equilibrium Constant. Suppose the reaction occurring in a galvanic cell is represented by



then from van't Hoff isotherm (chapter IX) we know that the thermodynamic potential change would be

$$\Delta G = -RT \ln K + RT \Sigma \nu \ln a \quad \dots \text{(XIII.6)}$$

where K is the equilibrium constant, and ' a '-terms denote the activities of the reactants and resultants.

If all the participants in the reaction are in standard state, their activities would be unity, the standard thermodynamic potential change would be given by

$$\Delta G^\circ = -RT \ln K \quad \dots \text{(XIII.7)}$$

Hence

$$\Delta G = \Delta G^\circ + RT \Sigma \nu \ln a \quad \dots \text{(XIII.8)}$$

The thermodynamic potential change in the cell reaction is the same as free energy change, the volume and pressure of the system remaining constant.

We have just seen also that ΔG is equal to the electrical energy output (equation XIII.2). If E is the e.m.f. of the given cell and E° the standard e.m.f. of the cell, then,

$$\Delta G = -n\mathcal{F}E \quad \dots \text{(XIII.9)}$$

and

$$\Delta G^\circ = -n\mathcal{F}E^\circ \quad \dots \text{(XIII.10)}$$

Substituting these relations in equation (XIII.7), we have

$$n\mathcal{F}E^\circ = RT \ln K$$

or

$$E^\circ = \frac{RT}{n\mathcal{F}} \ln K = 2.303 \frac{RT}{n\mathcal{F}} \log K \quad \dots \text{(XIII.11)}$$

And substituting in equation (XIII.8),

$$-n\mathcal{F}E = -n\mathcal{F}E^\circ + RT \Sigma \nu \ln a,$$

or

$$E = E^\circ - \frac{RT}{n\mathcal{F}} \Sigma \nu \ln a \quad \dots \text{(XIII.12)}$$

Also from (XIII.11 and 12), $E = \frac{2.303 RT}{n\bar{f}} \log K - \frac{2.303 RT}{n\bar{f}} \Sigma \nu \log a$... (XIII.13)

The quantity $\frac{2.303 RT}{\bar{f}}$ would occur very often in calculations of e.m.f. Its value for $T = 298^\circ K$ is $\frac{2.303 \times 8.32 \times 298}{96500} = 0.059$,

(R must be taken in joules). The values of this quantity at other temperatures are :

Temp.	0°C	10°C	25°C	30°C
$\frac{2.303 RT}{\bar{f}}$	0.0542	0.0562	0.0591	0.0602

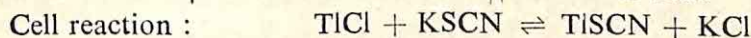
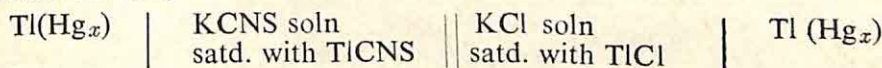
Hence at 25°C, $E^\circ = \frac{0.0591}{n} \log K$

$$E = E^\circ - \frac{0.0591}{n} \Sigma \nu \log a$$

and $E = \frac{0.0591}{n} \log K - \frac{0.0591}{n} \Sigma \nu \log a$... (XIII.14)

These are the different forms of what is commonly known as “Nernst equation” for galvanic cells. It is evident that determination of e.m.f. would permit the evaluation of equilibrium constant and *vice versa*.

The validity of this relation was tested experimentally first by Knupffer (1898) who studied the cell,



Since solid TiCl and TiSCN are present, their concentrations remain constant. From equation (XIII.13),

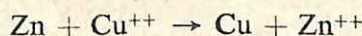
$$E = \frac{2.303 RT}{\bar{f}} \log K - \frac{2.303 RT}{\bar{f}} \log \frac{a_{\text{KCNS}}}{a_{\text{KCl}}} \dots (\text{since } n = 1)$$

$$\approx \frac{2.303 RT}{\bar{f}} \log K - \frac{2.303 RT}{\bar{f}} \log \frac{C_{\text{KCNS}}}{C_{\text{KCl}}}$$

At 20°C, the eqm. constant (K) of the process was found to be 1.24. The e.m.f. of the cell was then calculated to be 0.0051 and the e.m.f. experimentally observed was 0.0048 volts, (when the ratio $C_{\text{KCl}} : C_{\text{KSCN}} = 1.52$). The agreement is quite satisfactory.

A few illustrations of the application of Nernst equation are given here.

(i) The standard e.m.f. of the Daniell cell is 1.1 volts at 25°C, and the reaction is



$$\therefore K = \frac{a_{\text{Cu}} \times a_{\text{Zn}^{++}}}{a_{\text{Zn}} \times a_{\text{Cu}^{++}}} = \frac{a_{\text{Zn}^{++}}}{a_{\text{Cu}^{++}}} \quad (\text{since } a_{\text{Zn}} = a_{\text{Cu}} = 1)$$

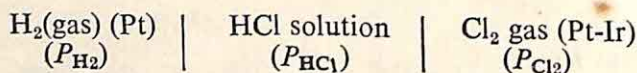
Now $E^\circ = \frac{RT}{n\bar{f}} \ln K = \frac{0.0591}{2} \log K$

i.e., $1.1 = \frac{0.0591}{2} \log K$, whence $K = 1.7 \times 10^{37}$

$\therefore$ At eqm. $a_{\text{Zn}^{++}} = 1.7 \times 10^{37} a_{\text{Cu}^{++}}$

In other words, the reaction practically proceeds to completion.

(ii) The equilibrium constant of the reaction $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}$ may be determined from the e.m.f. of the cell



The dilute HCl solution is in equilibrium with HCl-gas.

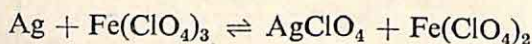
At 30°C , the e.m.f. of the cell was observed to be 1.01 volts when $P_{\text{HCl}} = 135$ mm, and $P_{\text{H}_2} = P_{\text{Cl}_2} = 620$ mm.

$$\text{Now } E = \frac{2.303 RT}{n\bar{f}} \log K - \frac{2.303 RT}{n\bar{f}} \log \frac{P_{\text{HCl}}^2}{P_{\text{Cl}_2} \times P_{\text{H}_2}}$$

$$\text{or } \log K = \frac{n\bar{f}E}{2.303 RT} + \log \frac{P_{\text{HCl}}^2}{P_{\text{Cl}_2} \times P_{\text{H}_2}}$$

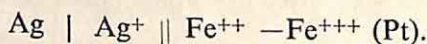
Since $n = 2$, $T = 303^\circ\text{K}$, using the pressures given, $K = 1.8 \times 10^{32}$

(iii) On the other hand from the equilibrium constant of a chemical process, the e.m.f. of a voltaic cell involving the corresponding reaction can be evaluated. For the reaction,



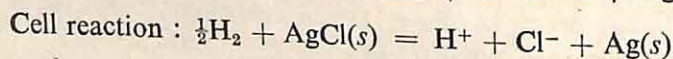
the eqm. constant at 25°C was found to be 0.50 after necessary corrections with Debye Law. (Schumb et al).

Let E° be the standard e.m.f. of the cell



$$\text{So that } E^\circ = \frac{2.303 RT}{n\bar{f}} \log (0.50) = 0.0591 \log (0.50) = -0.017 \text{ volts}$$

(iv) Again, consider a cell, $(\text{Pt})\text{H}_2 \mid \text{HCl soln} \mid \text{AgCl-Ag}$



$$\text{The e.m.f., } E = E^\circ - \frac{2.303 RT}{\bar{f}} \log \frac{a_{\text{H}^+} \cdot a_{\text{Cl}^-}}{\sqrt{a_{\text{H}_2}}}$$

If H_2 -gas be at unit pressure $a_{\text{H}_2} = 1$, at 25°C ,

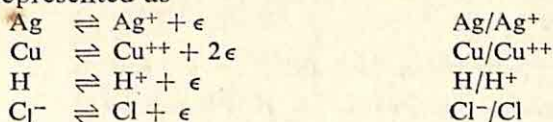
$$\begin{aligned} \therefore E &= E^\circ - 0.0591 \log (a_{\text{H}^+} \cdot a_{\text{Cl}^-}) \\ &= E^\circ - 0.0591 \log (m_{\pm} \gamma_{\pm})^2 = E^\circ - 0.1182 \log m_{\pm} \gamma_{\pm} \end{aligned}$$

$\gamma_{\pm}$ can be obtained using Debye Limiting Law. Hence a determination of E would enable us to evaluate E° , from which eqm. constant can be calculated.

XIII.5. Types of Single Electrodes. A galvanic cell must necessarily consist of at least two electrodes, positive and negative. As mentioned earlier, each of these electrodes is known as a *half-cell* or a *single electrode*. The process occurring in the cell ultimately causes in a given electrode transfer of electrons from the electrode to the electrolyte or *vice versa*, resulting into a flow of current when circuit is closed. The electrodes are usually formed by dipping a metal into an electrolyte and these may be classified into three broad types.

Type I. The simplest electrodes are formed when a metal or a non-metal is in contact with a solution containing its own ions. Thus silver immersed in silver nitrate solution, copper in copper sulphate solution, are common examples of this type. Similarly chlorine in contact with a chloride solution or hydrogen

in contact with an acid solution would also function as electrodes. The electrode processes may be represented as



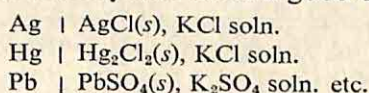
In the case of non-metal electrodes which are often non-conductors and sometimes gaseous, a special arrangement is needed for conduction. Usually a platinum foil or wire coated with platinum black is kept immersed in the solution and the non-metal gas is bubbled about it so that the Pt-black is fully saturated with adsorbed gas. The adsorbed molecules and their ions in solutions are thus brought in contact through the platinum. The Pt-black serves to establish equilibrium between the gas and its ions in solution and in fact facilitates electric contact. The electrodes are often represented as



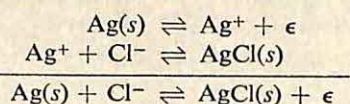
In some cases of metal-metal ion electrodes, such as those of potassium, sodium, calcium etc., the pure metals are too active to use them in aqueous solution of their ions. As such these are used in the form of their mercury amalgams, hence often called amalgam electrodes. The potentials of such electrodes would depend upon the activity of the metal in the amalgam used. The use of amalgam electrodes are often welcome in preference to the use of pure metals as equilibrium is attained readily and these are more readily reversible. The amalgam electrodes are often represented as



Type II. A metal with one of its sparingly soluble salts in contact with a solution having the same anion may also form a good electrode, e.g.,



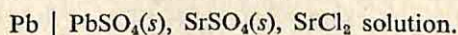
The electrode process is as follows. Consider the silver-silver chloride electrode. There are some silver ions in the solution though very small in view of low solubility of silver chloride. Hence Ag/Ag^+ ion system is there. As in type I, some silver ions will pass into solution as $\text{Ag} \rightleftharpoons \text{Ag}^+ + \epsilon$. Since the solution is saturated with AgCl , the silver ions produced will combine with Cl^- ions to restore solubility equilibrium, $\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl}(s)$. The net result is the removal of chloride ion from solution with electrons transferred to the metal.



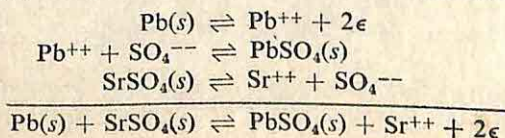
The electrode therefore is really reversible with respect to the anion *i.e.*, Cl^- ion. Other electrodes of this type also function in the same way. In the lead-lead sulphate electrode, the reaction is



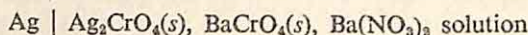
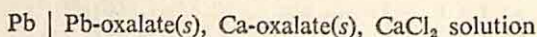
A modification of the arrangement shown above is sometimes used to obtain a metal-metal ion reversible electrode. In such cases, a metal in contact with one of its sparingly soluble salt together with another insoluble salt with a common anion is placed in the solution of a salt having a common cation as that of the latter salt. For example,



In this case when lead dissolves forming Pb^{++} ions, the latter is immediately removed as $\text{PbSO}_4(s)$. To maintain the solubility product more SrSO_4 would dissolve and ionise. The net process is

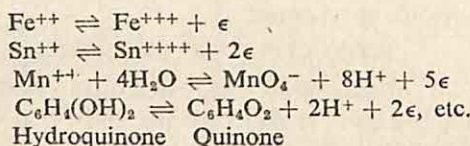


The system thus behaves as an electrode reversible with respect to Sr^{++} ions, which otherwise is difficult to obtain directly. In the same way, electrodes reversible with respect to Ca^{++} or Ba^{++} ions may be obtained, as



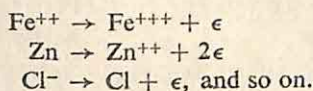
Type III. An inert metal, such as platinum, immersed in a solution containing a mixture of the oxidised and the reduced states of a system, constitutes an important type of an electrode.

Thus, a Pt-wire dipped in a mixture of the solutions of Fe^{++} and Fe^{+++} salts, or Sn^{++} and Sn^{++++} salts, etc. will serve as a single electrode. The reactions in such a case involve transfer of electrons between the oxidised and the reduced forms, e.g.,

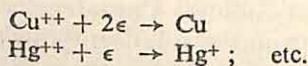


These electrodes are often mentioned as 'oxidation-reduction' electrodes.

Oxidation, in modern terminology, means liberation or giving up of electrons. Thus ferrous ion is oxidised to ferric ion and zinc atom is oxidised to Zn^{++} ion, Cl^- ion is oxidised to chlorine atom,



Reduction is the opposite process and it involves the acceptance or taking up of electrons, as Cu^{++} ions are reduced to Cu atoms or Hg^{++} ions are reduced to Hg^+ ions by taking up electrons,

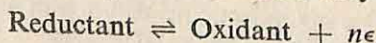


Thus, Fe^{+++} , Zn^{++} , Cu^{++} , Cl , Hg^{++} etc. are the oxidised states called *oxidants*, and Fe^{++} , Zn , Cu , Cl^- , Hg^+ etc. are the reduced states, called *reductants*.

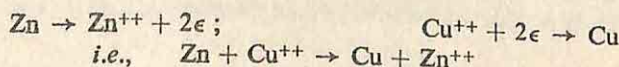
The three types of electrodes considered above are structurally different, but in every case, electrons are either liberated or taken up, the process being reversible. A reversible electrode therefore will involve an oxidant and a reductant. The process in the electrodes may be represented as

	Electrode Process	Oxidant	Reductant
Type I	$\text{Zn} \rightleftharpoons \text{Zn}^{++} + 2e$	Zn^{++}	Zn
Type II	$\text{Ag} + \text{Cl}^- \rightleftharpoons \text{AgCl} + e$	AgCl	Cl^-
Type III	$\text{Fe}^{++} \rightleftharpoons \text{Fe}^{+++} + e$	Fe^{+++}	Fe^{++}

Hence, in any electrode, the process involved may be expressed as :



When a galvanic cell yields electrical energy oxidation occurs at one electrode and reduction at the other. For example in the Daniell cell, while it gives current, zinc ionises at the negative electrode and copper ions are deposited at the positive.



Hence, oxidation occurs at the zinc electrode and reduction at the copper electrode. This is generally true for all reversible cells. The general convention is that the

electrode where oxidation occurs is regarded as the negative electrode and the electrode where reduction takes place is the positive electrode and the current flows from the latter to the former in the external circuit, Zn—ZnSO₄ solution // CuSO₄ solution—Cu.

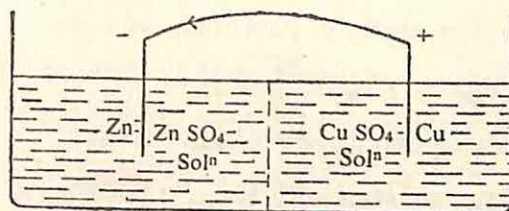


FIG. XIII.4a Daniell cell

It is the commonly adopted practice to put the negative electrode at the left while expressing a cell in writing.

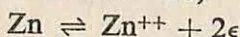
A metal is regarded as an assembly of metal ions and free electrons. When the metal is in contact with water, some metal ions enter into the liquid due to a tendency in the metal, called by Nernst as 'electrolytic solution tension'. As some metal ions leave the solid, the solid becomes negatively charged and the solution positively. In consequence, due to electrostatic force, any further transference of the metal ions is prevented and the ions, attracted by the negatively charged metal, remain near the metal surface forming a double layer. If the metal is placed in a solution containing its own ions, the metal ions from the solution in virtue of their osmotic pressure may enter into the metal rendering its surface positively charged. Again, by attraction now, the anions would flock near the positively charged metal surface and form a double layer. There is thus always a double layer at the contact of the electrode-metal and electrolyte. Hence, a difference of potential exists between the metal phase and the solution phase. This potential difference in the half-cell is called the *single electrode potential*. The transfer of metal ions from the solution to the metal would obviously depend upon the magnitude of the electrolytic solution tension of the metal and the osmotic pressure.

Due to the uncertainty of the physical significance of Nernst's electrolytic solution tension, the electrode potential is at present supposed to be due to the difference in the rates of two opposing processes, namely, the transfer of ions from the metal to the solution and the discharge of ions from the solution on the metal. If the rate of transfer of metal ions into solution be greater, there will be excess of electrons in the metal rendering it negative, which will attract +ve ions forming a double layer. If, on the other hand, the rate of discharge of ions from the solution to the metal be greater than that of the opposite process, the metal would be positive and it will attract negative anions forming a double layer. In any case, a double layer would be formed giving rise to electrical potential difference, which has been called the electrode potential. Similar conditions also apply to the non-metal or other electrodes.

The e.m.f. of a voltaic cell is really the algebraic sum of the two single electrode potentials. The liquid junction potential, if any, is not considered at the moment.

XIII.6. Single Electrode Potentials. The potential difference of the double layer formed at an electrode has been defined as 'single electrode potential'. There is also the equilibrium existing between the ions in the solution phase and the neutral atoms of the solid metal phase (or amalgam or inert metal conductor). The equilibrium, we have seen, is really between a reductant and an oxidant. We can thus apply the equation (XIII.12) to the electrode system.

(a) Let us take the *zinc-zinc ion electrode*,



If ξ_{Zn} be the electrode potential of zinc immersed in a solution having zinc ions of activity $a_{\text{Zn}^{++}}$, then, from equation (XIII.12),

$$\xi_{\text{Zn}} = \xi_{\text{Zn}}^0 - \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{++}}}{a_{\text{Zn}}} \quad \dots \text{(XIII.15)}$$

where ξ_{Zn}^0 is a constant and is equal to $\left(\xi^0 = \frac{RT}{nF} \ln K \right)$, vide equation (XIII.11).

We have simply applied the relation (XIII.12) to electrode reaction instead of the cell-reaction. a_e has been tacitly assumed to be unity.

$$\text{Hence,} \quad \xi_{\text{Zn}} = \xi_{\text{Zn}}^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{oxidant}}}{a_{\text{reductant}}} \quad \dots \text{(XIII.16)}$$

Moreover, since $a_{\text{Zn}} = 1$, (activity of pure zinc), we have

$$\xi_{\text{Zn}} = \xi_{\text{Zn}}^0 - \frac{RT}{n\mathcal{F}} \ln a_{\text{Zn}^{++}} \quad \dots \text{(XIII.17)}$$

When a solution having unit activity of Zn^{++} is used,

$$\xi_{\text{Zn}} = \xi_{\text{Zn}}^0 - \frac{RT}{n\mathcal{F}} \ln a_{\text{Zn}^{++}} = \xi_{\text{Zn}}^0$$

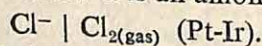
That is, ξ_{Zn}^0 is the electrode potential of the zinc electrode with the standard Zn^{++} ion solution of unit activity. ξ_{Zn}^0 is called the '*normal or standard electrode potential of zinc*'.

In a galvanic cell, there will be oxidation at one electrode by releasing electrons while at the other electrode reduction would occur. The potential (ξ) of the electrode where oxidation occurs is called the "*Oxidation potential of the electrode*". If the activity of the ion be unity then the said potential is the *standard oxidation potential*. On the other hand, the potential of the electrode, where reduction takes place, is termed its reduction potential. The magnitude of the reduction potential is equal to the oxidation potential with the sign reversed.

In a Daniell cell, $\text{Zn} | \text{Zn}^{++} || \text{Cu}^{++} | \text{Cu}$, oxidation takes place at the zinc electrode and if $a_{\text{Zn}^{++}} = 1$ then its standard oxidation potential is + 0.761 volts. But if we construct a cell with zinc and an amalgam of potassium as electrodes, $\text{K} | \text{K}^+ || \text{Zn}^{++} | \text{Zn}$, reduction of Zn^{++} would occur at the zinc electrode. With $a_{\text{Zn}^{++}} = 1$, the reduction potential of zinc here will be -0.761 volts. In other words during the passage of electricity when reduction occurs at the cathode, its potential would be opposite to its own oxidation potential. We shall presently see that all electrode potentials are assigned numerical values on the assumption of the potential of the standard hydrogen electrode as zero.

Let us now consider the potentials of some other single electrodes.

(b) *Chlorine Electrode*. It is an anion electrode,



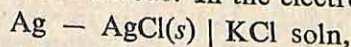
where the equilibrium is $\text{Cl}^- = \frac{1}{2}\text{Cl}_2 + e$

Hence, with equation (XIII.12),

$$\xi_{\text{Cl}_2} = \xi_{\text{Cl}_2}^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Cl}_2}}{a_{\text{Cl}^-}} = \xi_{\text{Cl}_2}^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{oxidant}}}{a_{\text{reductant}}}$$

The relation is the same as given in eqn. (XIII.16). $\xi_{\text{Cl}_2}^0$ is the normal oxidation potential of chlorine electrode when chlorine gas at unit pressure is in contact with Cl^- ion solution of unit activity.

(c) *Silver-Silver chloride Electrode*. In the electrode,



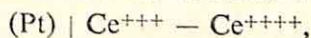
the overall process at the electrode is $\text{Ag} + \text{Cl}^- = \text{AgCl} + e$

$$\begin{aligned} \text{Applying eqn. (XIII.12), } \xi_{\text{Ag-AgCl}} &= \xi_{\text{Ag-AgCl}}^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{AgCl}}}{a_{\text{Ag}} \cdot a_{\text{Cl}^-}} \\ &= \xi_{\text{Ag-AgCl}}^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{AgCl}}}{a_{\text{Cl}^-}} \quad (\text{since } a_{\text{Ag}} = 1) \end{aligned}$$

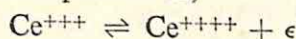
$$\text{or} \quad \xi_{\text{Ag-AgCl}} = \xi_{\text{Ag-AgCl}}^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{oxidant}}}{a_{\text{reductant}}}$$

the same form as seen earlier in equation (XIII.16). $\xi_{\text{Ag-AgCl}}^0$ is the normal oxidation potential of the electrode.

(d) *Oxidation-reduction or Redox electrode* : Take the electrode,



in which the equilibrium is expressed as,



So from eqn. (XIII.12)
$$\xi_{\text{redox}} = \xi^0_{\text{redox}} - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Ce}^{++++}}}{a_{\text{Ce}^{+++}}}$$

It is thus seen that the oxidation potential of the electrode again is

$$\xi_{\text{redox}} = \xi^0_{\text{redox}} - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{oxidant}}}{a_{\text{reductant}}}$$

Hence for all types of electrodes the oxidation potential (ξ) is represented as :

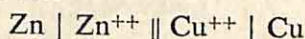
$$\xi = \xi^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{oxidant}}}{a_{\text{reductant}}} \quad \dots \text{(XIII.18)}$$

Next we may examine the relation between the electrode potentials (ξ) and the e.m.f. of the cell (E). The rule is :

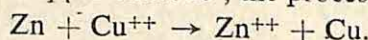
"The e.m.f. of a cell is the algebraic sum of the electrode potentials of the cell."

In every cell, oxidation occurs at the anode and reduction at the cathode. So, in computing the e.m.f. of the cell, take the *oxidation potential* of anode and the *reduction potential* of cathode. The reduction potential is the same as its oxidation potential with the sign changed. This is illustrated below.

(i) Take the Daniell cell



in which zinc is anode and copper cathode ; the process is



The e.m.f. of the cell is given by eqn. (XIII.12).

$$E = E^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Zn}^{++}} \cdot a_{\text{Cu}}}{a_{\text{Cu}^{++}} \cdot a_{\text{Zn}}} = E^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Zn}^{++}}}{a_{\text{Cu}^{++}}} \quad \dots \text{(X)}$$

The oxidation potential of zinc anode is

$$\xi_{\text{Zn}} = \xi^0_{\text{Zn}} - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Zn}^{++}}}{a_{\text{Zn}}} = \xi^0_{\text{Zn}} - \frac{RT}{n\mathcal{F}} \ln a_{\text{Zn}^{++}}$$

The oxidation potential of copper electrode is

$$\xi_{\text{Cu}} = \xi^0_{\text{Cu}} - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Cu}^{++}}}{a_{\text{Cu}}} = \xi^0_{\text{Cu}} - \frac{RT}{n\mathcal{F}} \ln a_{\text{Cu}^{++}}$$

Hence the reduction potential of copper cathode is

$$-\xi_{\text{Cu}} = - \left[\xi^0_{\text{Cu}} - \frac{RT}{n\mathcal{F}} \ln a_{\text{Cu}^{++}} \right]$$

The algebraic sum is

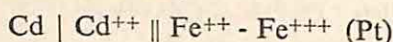
$$\begin{aligned} E &= \xi_{\text{Zn}} + (-\xi_{\text{Cu}}) \\ &= \xi^0_{\text{Zn}} - \frac{RT}{n\mathcal{F}} \ln a_{\text{Zn}^{++}} - \xi^0_{\text{Cu}} + \frac{RT}{n\mathcal{F}} \ln a_{\text{Cu}^{++}} \\ &= \left(\xi^0_{\text{Zn}} - \xi^0_{\text{Cu}} \right) - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Zn}^{++}}}{a_{\text{Cu}^{++}}} \\ &= E^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Zn}^{++}}}{a_{\text{Cu}^{++}}}, \end{aligned}$$

the same as in (X) above.

The normal e.m.f. of the cell likewise is the algebraic sum of the normal electrode potentials, i.e., $E^0 = \xi^0_{\text{Zn}} - \xi^0_{\text{Cu}}$.

Hence the e.m.f. of the cell can be computed from the electrode potentials.

(ii) Let us consider another cell,



in which it is found that Cd is the anode and $\text{Fe}^{++} - \text{Fe}^{+++}$ electrode functions as cathode ; the reaction is



The e.m.f. of the cell is

$$E = E^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Cd}^{++}} \cdot a_{\text{Fe}^{++}}^2}{a_{\text{Fe}^{+++}}^2} \quad (\text{since } a_{\text{Cd}} = 1) \quad \dots (\text{Y})$$

The oxidation potential of Cd-electrode is

$$\xi_{\text{Cd}} = \xi_{\text{Cd}}^0 - \frac{RT}{n\mathcal{F}} \ln a_{\text{Cd}^{++}}$$

The reduction potential of redox electrode ($\text{Fe}^{++} - \text{Fe}^{+++}$) is

$$- \xi_{\text{redox}} = - \left[\xi_{\text{redox}}^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Fe}^{+++}}^2}{a_{\text{Fe}^{++}}^2} \right]$$

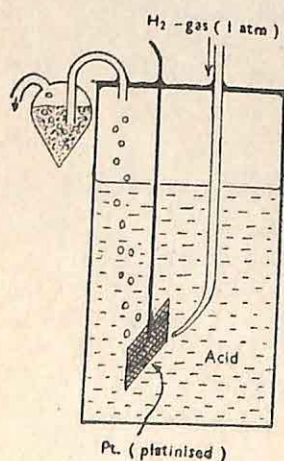
Hence, $E = \xi_{\text{Cd}} + (-\xi_{\text{redox}})$

$$\begin{aligned} &= \xi_{\text{Cd}}^0 - \frac{RT}{n\mathcal{F}} \ln a_{\text{Cd}^{++}} - \xi_{\text{redox}}^0 + \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Fe}^{+++}}^2}{a_{\text{Fe}^{++}}^2} \\ &= \left(\xi_{\text{Cd}}^0 - \xi_{\text{redox}}^0 \right) - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Cd}^{++}} \cdot a_{\text{Fe}^{++}}^2}{a_{\text{Fe}^{+++}}^2} \\ &= E^0 - \frac{RT}{n\mathcal{F}} \ln \frac{a_{\text{Cd}^{++}} \cdot a_{\text{Fe}^{++}}^2}{a_{\text{Fe}^{+++}}^2}, \end{aligned}$$

the same as in (Y) above.

If after the numerical computation the e.m.f. of the cell is found to be negative, it is to be understood that the process is actually reverse of what is assumed and the current flows opposite way. The anodes and cathodes are to be interchanged.

XIII.7. Standard Electrode Potentials. In order to assign numerical values to the electrode potentials, it is necessary to choose a standard electrode and assign an arbitrary value to the potential of the same. For this purpose the reference electrode is the *normal hydrogen electrode*, $\text{H}_2(\text{Pt})_{\text{gas}} \mid \text{H}^+ (a=1)$, in which pure hydrogen gas at unit pressure is kept in contact with solution containing H^+ -ion of unit activity through adsorption on Pt-black by continuous bubbling of the gas. A common laboratory arrangement of H_2 -electrode is shown in Fig. XIII.5. The potential of this normal hydrogen electrode is taken as zero at all temperatures. It should be emphasised that if the acid solution has H^+ ion activity other than unity, the electrode potential would no longer be zero. For



$$\xi_{\text{H}_2} = \xi_{\text{H}_2}^0 - \frac{RT}{n\mathcal{F}} \ln a_{\text{H}^+} = - \frac{RT}{n\mathcal{F}} \ln a_{\text{H}^+}$$

If $a_{\text{H}^+} \neq 1$; $\xi_{\text{H}_2} \neq 0$.

The potentials of other electrodes are expressed in reference to the normal hydrogen electrode. To evaluate the potential of any other single electrode, it

FIG. XIII.5 Hydrogen electrode

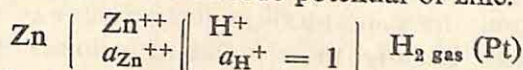
is necessary to couple it with standard or normal hydrogen electrode and the e.m.f. of the galvanic cell is measured potentiometrically. Since the e.m.f. of the cell is known and equal to the algebraic sum of the two electrode potentials, of which $\xi^0_{H_2}$ is zero, the potential of the other electrode is obtained. If ξ_x and $\xi^0_{H_2}$ are the oxidation potential of the electrode and the standard potential of hydrogen electrode respectively, the e.m.f. (E) of the cell will be given by the difference of the two, remembering that cathode potential would be negative ; i.e.,

$$E = \xi_x \sim \xi^0_{H_2}$$

Since $\xi^0_{H_2} = 0$, hence $E = \xi_x$

Let us take some examples.

(i) Determination of electrode potential of zinc. Arrange the cell,



in which zinc is the anode. The e.m.f. of this cell measured potentiometrically is suppose E . Then

$$E = \xi_{Zn} - \xi^0_{H_2} = \left[\xi^0_{Zn} - \frac{RT}{nF} \ln a_{Zn^{++}} \right] - 0 = \xi^0_{Zn} - \frac{RT}{nF} \ln a_{Zn^{++}}.$$

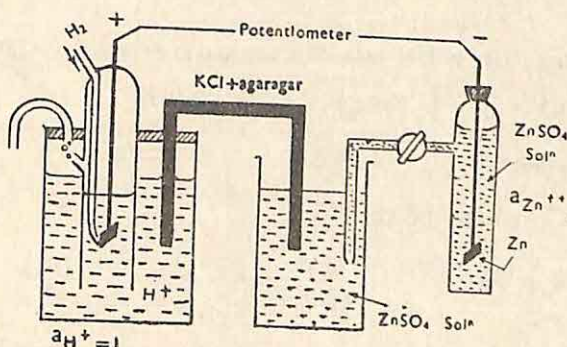


FIG. XIII.6 Det. of electrode potential $Zn \mid Zn^{++}$ from the e.m.f. of cell $Zn \mid Zn^{++} \parallel H^+ \mid H_2$

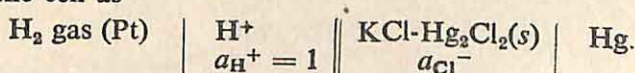
If the zinc sulphate solution taken has unit activity, then the measured e.m.f. of the cell would be the standard electrode potential of zinc, ξ^0_{Zn} . Otherwise, $a_{Zn^{++}}$ the activity of the Zn^{++} is separately measured to obtain the value of ξ^0_{Zn} .

The potentials of other electrodes are evaluated in the same way by coupling with a normal hydrogen electrode.

(b) Determination of potential of calomel electrode,



Arrange the cell as



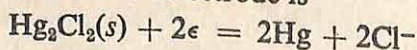
in which calomel electrode is the cathode.

The e.m.f. E of this cell is $E = \xi^0_{H_2} + (-\xi_{Cal})$

or $E = -\xi_{Cal}$

where ξ_{Cal} is the oxidation potential of the calomel electrode.

The process at the calomel electrode is



$$\therefore \xi_{Cal} = \xi^0_{Cal} - \frac{RT}{2F} \ln a^2_{Cl^-}$$

$$\therefore E = -\xi^0_{Cal} + \frac{RT}{2F} \ln a^2_{Cl^-}$$

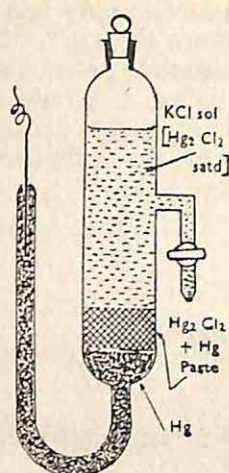


FIG. XIII.7 Calomel electrode

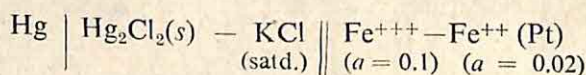
If a_{Cl^-} , activity of the Cl^- ion in the KCl solution used, be separately determined and E is potentiometrically measured, the standard potential of calomel electrode, ξ_{Cal}^0 is known.

In fact the use of standard H_2 -electrode is often inconvenient as considerable difficulties arise in its preparation. Calomel electrodes are extensively used as a secondary reference electrode. The calomel electrodes are easily prepared and these attain reversibility rapidly. It has been seen that its potential depends upon the concentration (or activity) of KCl solution used. Usually three standard calomel electrodes are used in the laboratory with saturated, 1 normal and 0.1 normal KCl solutions. The standard electrode potentials are tabled below. The common form of the electrode is shown in Fig. XIII.7.

TABLE : THE POTENTIALS OF CALOMEL ELECTRODE AT 25°C

Conc. of KCl	Saturated	1.0 N	0.1 N
Electrode potential	-0.2415	-0.2800	-0.3338

To illustrate : Consider the cell



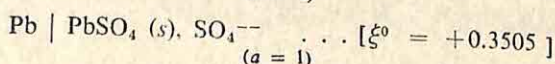
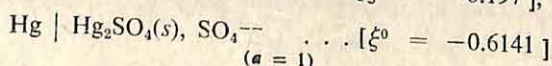
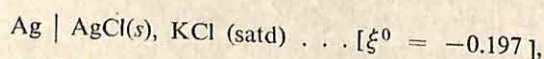
in which calomel electrode is the anode, to determine the potential of the oxidation-reduction ($\text{Fe}^{++} - \text{Fe}^{+++}$) electrode. The e.m.f. of the cell was measured and found to be 0.5707 volts. Now, the $\xi_{\text{Cal}} = -0.2415$ for saturated KCl-calomel electrode.

$$\begin{aligned} \therefore E &= \xi_{\text{Cal}} + (-\xi_{\text{redox}}) \\ &= \xi_{\text{Cal}} - \left[\xi_{\text{redox}}^0 - \frac{RT}{f} \ln \frac{a_{\text{Fe}^{+++}}}{a_{\text{Fe}^{++}}} \right] \\ &= \xi_{\text{Cal}} - \left[\xi_{\text{redox}}^0 - 0.0591 \log \frac{0.1}{0.02} \right] \end{aligned}$$

$$\therefore 0.5705 = -0.2415 - \xi_{\text{redox}}^0 + 0.0410$$

$$\text{whence } \xi_{\text{Fe}^{+++} - \text{Fe}^{++}}^0 = -0.771 \text{ volts.}$$

Thus an electrode potential can be obtained by coupling it with a calomel electrode instead of a normal hydrogen electrode. Other subsidiary reference electrodes are also in use, such as,



In the table appended below, the standard oxidation potentials of different electrodes are given. The electrodes at the top of the Table have a greater tendency to give up electrons. If a cell is built up with two electrodes from this list, one

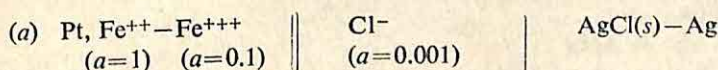
which is above in the list will be the anode. The plus and minus signs arise as we have given arbitrarily a zero value to the normal H_2 -electrode. If we put electrode potential of normal H_2 -electrode as 2 volts, the magnitude of every other electrode-potential would increase by two volts.

TABLE : STANDARD OXIDATION POTENTIALS (AT 25°C) OF SINGLE ELECTRODE (HYDROGEN SCALE)

Electrode	Electrode Reaction	Electrode Potential ξ° (volts.)
K K^+	$K = K^+ + e$	+ 2.925
Na Na^+	$Na = Na^+ + e$	+ 2.714
Mg Mg^{++}	$Mg = Mg^{++} + 2e$	+ 2.34
Zn Zn^{++}	$Zn = Zn^{++} + 2e$	+ 0.761
Fe Fe^{++}	$Fe = Fe^{++} + 2e$	+ 0.441
(Pt) $Cr^{++} - Cr^{+++}$	$Cr^{++} = Cr^{+++} + e$	+ 0.410
Cd Cd^{++}	$Cd = Cd^{++} + 2e$	+ 0.402
Co Co^{++}	$Co = Co^{++} + 2e$	+ 0.280
Ni Ni^{++}	$Ni = Ni^{++} + 2e$	+ 0.240
Ag $AgI(s) / I^-$	$Ag + I^- = AgI + e$	+ 0.152
Sn Sn^{++}	$Sn = Sn^{++} + 2e$	+ 0.140
Pb Pb^{++}	$Pb = Pb^{++} + 2e$	+ 0.126
(Pt) $\frac{1}{2}H_2(g) H^+$	$\frac{1}{2}H_2 = H^+ + e$	0.000
(Pt) $Sn^{++} - Sn^{++++}$	$Sn^{++} = Sn^{++++} + 2e$	-- 0.15
Ag $AgCl(s) / Cl^-$	$Ag + Cl^- = AgCl + e$	-- 0.2223
Hg $HgCl_2(s) / Cl^-$	$2Hg + 2Cl^- = Hg_2Cl_2 + 2e$	-- 0.2680
Cu Cu^{++}	$Cu = Cu^{++} + 2e$	-- 0.337
$I_2 I^-$	$2I^- = I_2 + 2e$	-- 0.535
(Pt) $Fe^{++} - Fe^{+++}$	$Fe^{++} = Fe^{+++} + e$	-- 0.771
Ag Ag^+	$Ag = Ag^+ + e$	-- 0.799
$Br_2 Br^-$	$2Br^- = Br_2 + 2e$	-- 1.0652
(Pt) $Tl^+ Tl^{+++}$	$Tl^+ = Tl^{+++} + 2e$	-- 1.250
Au Au^{+++}	$Au = Au^{+++} + 3e$	-- 1.300
$Cl_2 Cl^-$	$2Cl^- = Cl_2 + 2e$	-- 1.359
(Pt) $Ce^{---} - Ce^{++++}$	$Ce^{+++} = Ce^{++++} + e$	-- 1.610

Some Simple Calculations from Electrode Potential Values.

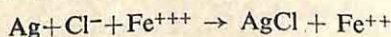
(i) Compute the e.m.f. of the following cells :



$$(a) \quad \xi_{Fe^{++} - Fe^{+++}} = \xi_{Fe^{++} - Fe^{+++}}^0 - \frac{RT}{f} \ln \frac{a_{Fe^{+++}}}{a_{Fe^{++}}} \\ = -0.771 - 0.059 \log \frac{0.1}{1.0} = -0.7120$$

$$\xi_{Ag - AgCl} = \xi_{Ag - AgCl}^0 - \frac{RT}{f} \ln \frac{1}{a_{Cl^-}} \\ = -0.223 - 0.059 \log \frac{1}{10^{-3}} = -0.3995.$$

The standard ξ^0 values are taken from the table. Obviously $Ag - AgCl$ electrode would be the anode and the spontaneous reaction is



The e.m.f. of the cell is

$$E = \xi_{Ag - AgCl} - \xi_{Fe^{++} - Fe^{+++}} \\ = -0.3995 - (-0.7120) = 0.3125 \text{ volts.}$$

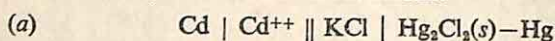
$$(b) \quad \xi_{Ag} = \xi^{\circ}_{Ag} - 0.059 \log (.01) = -0.799 + 0.118$$

$$\xi_{Zn} = \xi^{\circ}_{Zn} - \frac{0.059}{2} \log (0.1) = 0.762 + 0.029$$

Hence Zn-electrode will act as anode. The e.m.f. of the cell is

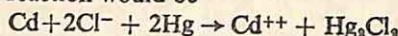
$$\begin{aligned} E &= E^{\circ} - \frac{RT}{2f} \ln \frac{a_{Zn^{++}}}{a_{Ag^+}^2} \\ &= (\xi^{\circ}_{Zn} - \xi^{\circ}_{Ag}) - \frac{0.059}{2} \log \frac{0.1}{(0.01)^2} \\ &= (0.762 + 0.799) - 0.089 = 1.472 \text{ volts} \end{aligned}$$

(ii) Write the cell reactions of the following cells and find out the free energy changes in the reactions involved, under standard conditions.



From the tables, $\xi^{\circ}_{Cd} = +0.402$, and $\xi^{\circ}_{\text{calomel}} = -0.2680$

Hence the spontaneous reaction would be

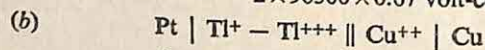


The e.m.f. of the cell is

$$E^{\circ} = \xi^{\circ}_{Cd} - \xi^{\circ}_{\text{Cal}} = +0.402 - (-0.2680) = 0.670 \text{ volts}$$

The free energy change $\Delta F^{\circ} = -n\mathcal{F}E^{\circ}$

$$= -2 \times 96500 \times 0.67 \text{ volt-coulombs} = -129.3 \times 10^3 \text{ joules}$$



$$\xi^{\circ}_{\text{Ti}^+/\text{Ti}^{+++}} = -1.250, \text{ and } \xi^{\circ}_{\text{Cu}} = -0.337$$

Since ξ°_{Cu} is higher, the copper electrode would be the anode and the cell reaction would be



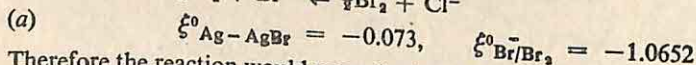
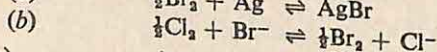
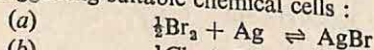
The standard e.m.f. of the cell is

$$E^{\circ} = \xi^{\circ}_{\text{Cu}} - \xi^{\circ}_{\text{Ti}^+/\text{Ti}^{+++}} = -0.337 - (-1.250) = 0.913 \text{ volts}$$

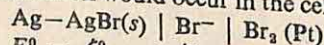
$\therefore$ Free energy change $\Delta F^{\circ} = -n\mathcal{F}E^{\circ}$

$$= \frac{-2 \times 96500 \times 0.913}{4.2} \text{ calories} = -41.95 \text{ Kcals.}$$

(iii) Calculate the standard free energy change and eqm. constants of the following reactions after suggesting suitable chemical cells :



Therefore the reaction would occur in the cell



$$\therefore E^{\circ} = \xi^{\circ}_{\text{AgBr}} - \xi^{\circ}_{\text{Br}_2} = -0.073 - (-1.0652) = 0.992 \text{ volts}$$

$$\therefore \Delta G = -n\mathcal{F}E^{\circ} = -96500 \times 0.992 \text{ volt-coulombs} = -22.9 \text{ Kcals.}$$

And since
$$E^{\circ} = \frac{RT}{n\mathcal{F}} \ln K = \frac{0.059}{1} \log K, \text{ at } 25^{\circ}\text{C}$$

$$\therefore \log K = \frac{0.992}{0.059}, \text{ whence } K = 6.46 \times 10^{16}$$

(b) Suitable cell for this reaction would be

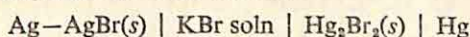


$$\begin{aligned} \text{The e.m.f. would be } E^{\circ} &= \xi^{\circ}_{\text{Br}_2} - \xi^{\circ}_{\text{Cl}_2} \\ &= -1.0652 - (-1.359) = 0.294 \text{ volts} \end{aligned}$$

$$\therefore \Delta F^{\circ} = -n\mathcal{F}E^{\circ} = \frac{-96500 \times 0.294}{4.2} = -6754 \text{ cal.}$$

And
$$\log K = \frac{E^{\circ}}{0.059} = \frac{0.294}{0.059}, \text{ whence } K = 1.0 \times 10^5 \text{ at } 25^{\circ}\text{C}$$

(iv) It is easy to evaluate the heat of reaction, entropy-change, etc. from a study of e.m.f. of cells at different temperatures. Take the cell,



The measured e.m.f.'s are 0.06839 at 25°C and 0.07048 at 30°C. Calculate, after stating the reaction involved, the values of the heat of reaction, free-energy change and entropy-change of the process.

The reaction may be represented as $2\text{Ag} + \text{Hg}_2\text{Br}_2 \rightleftharpoons 2\text{AgBr} + 2\text{Hg}$

$$\frac{dE}{dT} = \frac{1}{8} [0.07048 - 0.06839] = 4.2 \times 10^{-4}$$

$$\text{Hence } \Delta S = n\mathcal{F} \frac{dE}{dT} = \frac{2 \times 96500 \times 4.2 \times 10^{-4}}{4.2} = 19.3 \text{ e.u.}$$

$$\text{We have also, } \Delta G = -n\mathcal{F}E = -\frac{2 \times 96500 \times 0.06839}{4.2} = -3143 \text{ cal.}$$

$$\text{The heat of reaction } \Delta H = \Delta G + T\Delta S = -3143 + 298 \times 19.3 = 2808 \text{ cal.}$$

(v) The standard potentials for the electrodes $\text{Hg} \mid \text{Hg}_2^{++}$ and $\text{Hg} \mid \text{Hg}^{++}$ are -0.799 and -0.855 volts at 25°C. Calculate the equilibrium constant for the reaction: $\text{Hg} + \text{Hg}^{++} \rightleftharpoons \text{Hg}_2^{++}$.

Construct the cell, $\text{Hg} \mid \text{Hg}_2^{++} \parallel \text{Hg}^{++} \mid \text{Hg}$.

The anodic process is $2\text{Hg} \rightarrow \text{Hg}_2^{++} + 2e^-$; $\xi^0_{\text{Hg} \mid \text{Hg}_2^{++}} = -0.799$

The cathodic process is $\text{Hg}^{++} + 2e^- \rightarrow \text{Hg}$; $\xi^0_{\text{Hg} \mid \text{Hg}^{++}} = -(-0.855)$

Cell reaction: $\text{Hg} + \text{Hg}^{++} \rightleftharpoons \text{Hg}_2^{++}$ $E^0 = +0.056$

$$\text{Now } E^0 = \frac{RT}{2\mathcal{F}} \ln \frac{a_{\text{Hg}_2}}{a_{\text{Hg}} \cdot a_{\text{Hg}^{++}}} = \frac{RT}{2\mathcal{F}} \ln K$$

$$\text{or } 0.056 = \frac{0.059}{2} \log K, \quad \text{whence } K = 79.07$$

XIII.8. Applications of Electrode Potentials. We have seen how with the help of electrode potentials and e.m.f. of cells it is possible to evaluate equilibrium constant, heat of reaction or free energy change of processes.

We shall see later in studying the ionic equilibria that e.m.f. measurements contribute significantly in the determination of H^+ -ion concentrations, solubility products, hydrolytic constants, etc. In this section only a few general applications of electrode potential measurement will be illustrated.

1. Determination of Valence of an Ion. By coupling with a reference electrode, let the potential (ξ_1) of an electrode be determined when the activity of the reversible ion in solution is a_1 . By repeating the measurement with a solution having activity $\frac{1}{10} a_1$, suppose the e.m.f. is ξ_2 . Then

$$\xi_1 = \xi^0 - \frac{0.059}{n} \log a_1 \quad \xi_2 = \xi^0 - \frac{0.059}{n} \log \frac{a_1}{10}$$

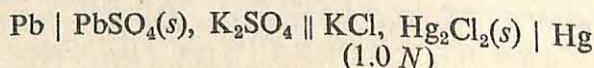
$$\text{Subtracting } \xi_2 - \xi_1 = \frac{0.059}{n} \log 10 = \frac{0.059}{n}$$

That is, ten-fold change in activity will produce a change of $0.059/n$ volts in electrode-potential.

$$\text{Rewriting } n = 0.059/(\xi_2 - \xi_1)$$

This has been found to hold generally in all cases. In dealing with reversible mercury electrodes, a ten-fold rise in the concentration of mercurous nitrate showed a change of 0.029 volts in the electrode potential. Hence $n = 2$, i.e., mercurous ions are bivalent Hg_2^{++} .

2. Determination of Ionic Activity. From a determination of the electrode potential (ξ), the activity of the reversible ion in the electrolyte may be obtained at least approximately. This is especially permissible when the electrolyte is sparingly soluble. Let us consider the cell,



The e.m.f. E of this cell is experimentally measured, which as usual is the sum of the oxidation potential of the $\text{Pb} \mid \text{PbSO}_4(s), \text{K}_2\text{SO}_4$ electrode and the reduction

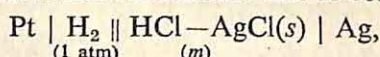
potential of calomel electrode. Since $\text{Pb} \mid \text{PbSO}_4(s), \text{K}_2\text{SO}_4$ electrode can also be deemed as a Pb/Pb^{++} electrode as described earlier, the observed e.m.f. can be expressed as

$$E = \xi_{\text{Pb}} + (-\xi_{\text{cal}}) = \xi_{\text{Pb}}^0 - \frac{RT}{2f} \ln a_{\text{Pb}^{++}} + 0.28, \text{ at } 25^\circ\text{C}$$

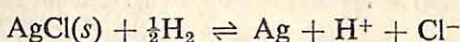
$$\text{or } \frac{RT}{2f} \ln a_{\text{Pb}^{++}} = \xi_{\text{Pb}}^0 + 0.28 - E$$

Inserting the value of ξ_{Pb}^0 from the table, the activity of Pb^{++} in the PbSO_4 -saturated solution of K_2SO_4 can be obtained.

3. Determination of Activity Coefficient. The activity coefficients can also be obtained from e.m.f. measurements. Let us consider the cell



i.e., Ag-AgCl electrode coupled with a hydrogen electrode (H_2 passed at 1 atm.). The cell reaction is



The e.m.f. of the cell is

$$\begin{aligned} E &= E^0 - \frac{RT}{f} \ln a_{\text{H}^+} a_{\text{Cl}^-} \\ &= E^0 - \frac{RT}{f} \ln a_{\pm}^2 \end{aligned}$$

where $a_{\pm}$ is the mean activity of the hydrochloric acid. Further we can substitute $a_{\pm}^2$ by $(\gamma_{\pm}m)^2$, where $\gamma_{\pm}$ is the mean activity coefficient.

$$\begin{aligned} \therefore E &= E^0 - \frac{2RT}{f} \ln (\gamma_{\pm}m) \\ &= E^0 - \frac{2RT}{f} \ln m - \frac{2RT}{f} \ln \gamma_{\pm} \\ &= E^0 - 0.118 \log m - 0.118 \log \gamma_{\pm} \end{aligned}$$

That is, $E + 0.118 \log m = E^0 - 0.118 \log \gamma_{\pm}$. . . (XIII.19)

The e.m.f. (E) of the cell using different concentration of HCl is measured. For very dilute solutions where Debye-Hückel limiting law is permitted, $\log \gamma_{\pm}$ is proportional to $\sqrt{m}$, since it is a uni-univalent electrolyte. That is, at low concentrations of HCl,

$$E + 0.118 \log m = E^0 - 0.118 (0.5) m^{\frac{1}{2}}$$

The quantity on the left-hand side ($E + 0.118 \log m$) is plotted against $\sqrt{m}$ and a linear graph is obtained at low concentrations (Fig. XIII.8). The straight line is extrapolated to $m = 0$, the intercept gives E^0 . When an accurate value of E^0 is known, the e.m.f. values of the cell at any other concentration gives the mean activity coefficients ($\gamma_{\pm}$) from equation XIII.19. The method, which can be used with other electrolytes also, is employed both for finding the normal e.m.f. or electrode potential as also the mean activity coefficient.

4. Potentiometric Titrations. Electrometric measurement provides a very important method for estimations in analytical chemistry. Different types of titration are carried out in presence of suitable electrodes and the variation of electrode potentials leads to the detection of the end-point of the reaction. The potentiometric titrations are of three types: (i) Precipitation reactions (ii) Oxidation-reduction reactions (iii) Acid-Base neutralisation reactions.

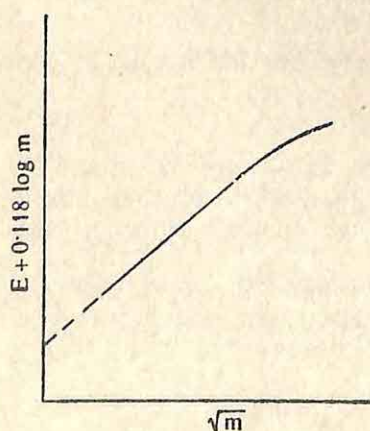
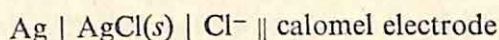


FIG. XIII.8 Det. of activity coefficient

(i) *Precipitation Reactions.* As an illustration, we may consider the estimation of chlorides by potentiometric titration with silver nitrate solution. A known volume of NaCl solution is taken in a beaker in which is inserted a clean silver wire to act as an electrode, called 'indicator' electrode. From a burette the titrant AgNO_3 is added in small amounts. As silver chloride is formed there, we have a reversible electrode $\text{Ag} \mid \text{AgCl}(s) \mid \text{Cl}^-$. This is coupled with a reference electrode say calomel electrode, i.e.,



The e.m.f. of the cell is given by

$$E = \xi_{\text{Ag}} - \xi_{\text{Cal}} = \xi_{\text{Ag}}^0 - \frac{RT}{f} \ln a_{\text{Ag}^+} - \xi_{\text{Cal}}$$

or
$$E = (\xi_{\text{Ag}}^0 - \xi_{\text{Cal}}) - \frac{RT}{f} \ln a_{\text{Ag}^+}$$

To simplify the treatment if we replace activity by concentration, then the approximate e.m.f. at 25°C would be

$$E = \text{constant} - 0.059 \log C_{\text{Ag}^+}$$

The solubility of AgCl is quite small, the concentration of Ag^+ ions in solution will change very slightly with the progress of the titration and hence the e.m.f. of the cell will change but little. But when the equivalence point is reached, even a drop of AgNO_3 added would bring about a large increase in the silver ion concentration and therefore a sharp change in the e.m.f. of the cell. In other words, when the sharp change in e.m.f. is detected, the end-point is reached. A plot of e.m.f. of the cell against the volumes of AgNO_3 solution added is shown in Fig. XIII.9a, from which the sudden change in slope is clearly noticed. The end-point is thus easy to detect. If the differential change in e.m.f. with volume be plotted against the volume of titre added, a still better indication of the end-point is obtained as in Fig. XIII.9b. This method can be easily extended to other titrations where precipitations occur. The indicator electrode has to be suitably chosen.

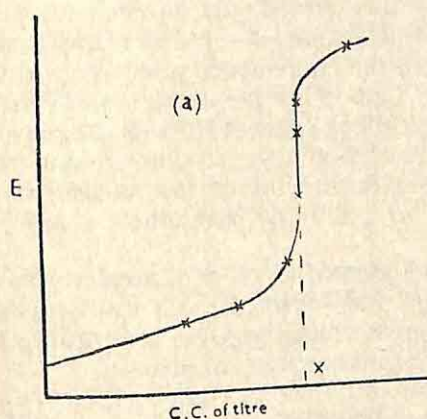


FIG. XIII.9a Potentiometric titration

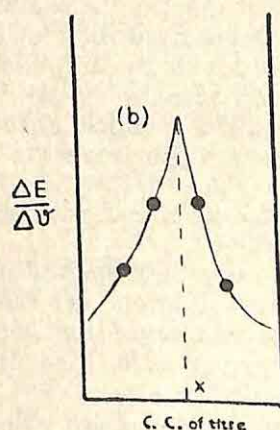
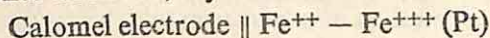


FIG. XIII.9b Det. of end point of titration

(ii) *Oxidation-Reduction Reactions.* As an illustrative example, let us consider the titration of an acidified ferrous sulphate solution with an oxidising agent, say a dichromate solution. A known volume of the ferrous salt solution is taken in a beaker and a Pt-wire is inserted. The titre $\text{K}_2\text{Cr}_2\text{O}_7$ solution is added from a burette. At any instant during the titration, we have a mixture of Fe^{++} and Fe^{+++}

ions with a Pt-wire in it and this forms a reversible electrode. This electrode is coupled with a reference electrode, say a calomel electrode, to form the cell,



Its e.m.f. would be $E = \xi_{\text{Cal}} - \xi_{\text{Fe}^{++} - \text{Fe}^{+++}}$

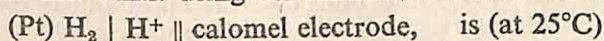
$$= \xi_{\text{Cal}} - \xi_{\text{Fe}^{++} - \text{Fe}^{+++}}^0 + \frac{RT}{f} \ln \frac{a_{\text{Fe}^{+++}}}{a_{\text{Fe}^{++}}}$$

Replacing activity by concentration, the e.m.f. at 25°C would be

$$E \approx \text{constant} + 0.059 \log \frac{C_{\text{Fe}^{+++}}}{C_{\text{Fe}^{++}}}$$

The progressive addition will cause a change in the e.m.f. of the cell as the ratio $C_{\text{Fe}^{+++}}/C_{\text{Fe}^{++}}$ increases, till an equilibrium is attained. The concentration of Fe^{++} ions will be ultimately extremely small but not zero. If the e.m.f. of the cell is plotted against the titre added, the curve will show its greatest slope when the equivalence point is reached. From an observation of the greatest slope, *i.e.*, sharp change in e.m.f., the end-pt of the reaction can be easily located. It is easily seen that before the end point is reached, the potentials are governed by the titrated system ($\text{Fe}^{++} - \text{Fe}^{+++}$ system). But when equivalence point is passed and excess of dichromate is added, the potentials are mainly determined by the titrant system ($\text{Cr}^{+++} - \text{Cr}_2\text{O}_7^{--}$ system). The sharpness of the e.m.f.-change will depend upon the difference of the standard potentials of the redox electrodes. If the standard potentials of the two systems are close enough the end-point will not be sharp.

(iii) *Acid-Base Reactions.* The electrometric titration of an acid by a base follows the same pattern as in the other two cases just discussed. In the acid solution is inserted a hydrogen electrode and this is coupled with a reference calomel electrode. The e.m.f. using concentration instead of activity of the cell,



$$E = \xi_{\text{H}_2} - \xi_{\text{Cal}} = (\xi_{\text{H}_2}^0 - \xi_{\text{Cal}}) - 0.059 \log C_{\text{H}^+}$$

The negative of the logarithm of conc. of H^+ ions is called the pH of the solution, *i.e.*, $-\log C_{\text{H}^+} = \text{pH}$.

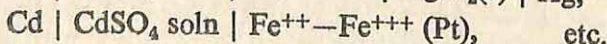
Hence

$$E = \text{constant} + 0.059 \text{ pH.}$$

With successive addition of alkali, the C_{H^+} will decrease *i.e.*, pH or e.m.f. of the cell will progressively change. By measuring the e.m.f. after each addition and plotting it against the volume of titre added, the equivalence point can be detected. It is observed that e.m.f. (or pH) changes relatively slowly in the beginning, then more rapidly, and then when the equivalence point is approached there is a very sharp increase in the e.m.f. This helps the detection of the end-point. When excess alkali is added, the change in pH again is slow or the curve tapers off. This is thus exactly comparable to curves of potentiometric titration of precipitation reactions (cf. Fig. XIII.9a). A detailed discussion of this measurement will be made in a later section in connection with the "determination of pH" by potentiometric method.

The potentiometric method of acid-base titration is particularly advantageous when the given solutions are coloured and indicators are not useful. It is also advantageously employed in titrations of polybasic acids, or in titrations of mixtures of weak and strong acids. [See 'dissociation constant of acids'.]

XIII.9. Liquid Junction Potentials : Chemical Cells with Transference. In chemical cells of the type,



two different solutions come in contact. There indeed is a junction of the two solutions from the two half-cells. The ions present on either side of the junction have a tendency to diffuse into the other side. The speeds of the different ions of

the two electrolytes, even those of cations and anions of the same electrolyte, are different. The result is that the faster ions move across the boundary ahead of the slower. So one side of the boundary becomes positively charged and the other negatively. That is, an electrical double layer is formed at the junction of the two liquids. The attraction between the two opposite charges prevents any appreciable separation of anions from cations. At the junction of two electrolytes therefore exists a potential difference, called *liquid junction potential* (ξ_j). Its magnitude depends upon the relative velocities of migration of the ions. Even if the same electrolyte be present in the two half-cells at different concentrations, the junction potential will arise due to the difference in the speeds of anions and cations.

In the treatment of chemical cells so far we have not taken into account the liquid junction potential (ξ_j). The e.m.f. of the cell has been computed from the algebraic sum of the two single electrode potentials, ignoring the junction potential.

The evaluation of the liquid junction potential in chemical cells is quite complicated. Planck, Henderson and others derived different expressions for ξ_j , based on the speed and concentration of the ions. Henderson's formula for ξ_j for electrolytes having various ions in contact is given by

$$\xi_j = \frac{RT}{\mathcal{F}} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U'_1 + V'_1) - (U'_2 + V'_2)} \ln \frac{U'_1 + V'_1}{U'_2 + V'_2} \quad \dots \text{(XIII.20)}$$

in which

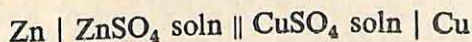
$$\begin{aligned} U_1 &= u_1c_1 + u_2c_2 + \dots & U'_1 &= u_1n_1c_1 + u_2n_2c_2 + \dots \\ V_1 &= v_1c_1 + v_2c_2 + \dots & V'_1 &= v_1n_1c_1 + v_2n_2c_2 + \dots \end{aligned}$$

where u and v terms are velocities of cations, anions, n -terms are valences, and c -terms are concentration of ions in one electrolyte. Similar expressions hold for U_2, U'_2, V'_2 for the ions in the other solution in contact. The theoretical treatment is too involved to be discussed in this text.*

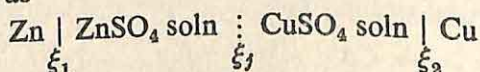
But in the construction of the chemical cells which we have dealt with earlier, the liquid junction potential has actually been eliminated and thus no error has crept in our calculations. There are several ways of eliminating ξ_j , but the most commonly used method is through the insertion of a strong solution of KCl or NH_4NO_3 in between the two half-cells. This is usually mentioned as insertion of a "salt-bridge". These salts are chosen, for, in these the speeds of cations and anions are almost equal. In actual construction, the liquid terminals of the two half-cells may be inserted in a beaker containing a concentrated solution of KCl. Or a tube filled with agar-agar jelly saturated with KCl may be used to connect the liquids in the two half-cells as in Fig. XIII.6.

It is tacitly assumed that junction potential difference between KCl and 1st electrolyte acts in opposition to the junction potential difference between KCl and 2nd electrolyte and the two are almost counterbalanced, so that the effective liquid junction potential is practically nil. It is difficult to say how far this assumption is justified. But the empirical fact remains that the e.m.f. determined with the use of salt-bridge agrees well with the calculated values. The salt bridges have come into extensive application and are regarded conventionally to eliminate ξ_j completely.

When the junction potential is eliminated, it is customary to write a cell with two vertical lines in between the two electrolytes, e.g.,



But if ξ_j is not eliminated, only one line or preferably a dotted line is given in between two solutions, as



Such cells are called *chemical cells with transference* and so,

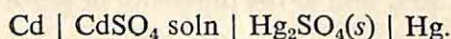
$$E = \xi_1 - \xi_2 + \xi_j \quad \dots \text{(XIII.21)}$$

* Physikal chem, 1907, 59, 118 ; 1908, 63, 325.

Where the liquid junction potential is eliminated, the cell is known as *chemical cell without transference*, so that

$$E = \xi_1 - \xi_2$$

Chemical cells without transference may also be constructed by using a single electrolyte such that one electrode is reversible with respect to the cation of the electrolyte and the other electrode reversible with respect to the anion. Thus if CdSO_4 solution is the electrolyte one electrode should be cadmium and the other electrode $\text{Hg}_2\text{SO}_4\text{--Hg}$. The cell is



Similarly, $\text{H}_2(g), \text{Pt} \mid \text{HCl solution} \mid \text{AgCl}(s), \text{Ag}$

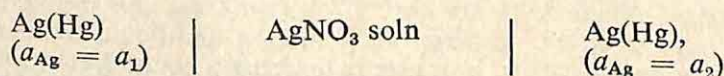
or $\text{Zn} \mid \text{ZnBr}_2 \text{ solution} \mid \text{Hg}_2\text{Br}_2(s) \mid \text{Hg}$

are examples of chemical cells without transference *i.e.*, without liquid junction potential.

CONCENTRATION CELLS

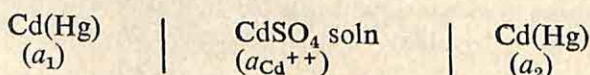
The e.m.f. in chemical cells is a consequence of the chemical reactions occurring in the cell. But there is another type of cells in which the e.m.f. arises not due to any chemical reaction but due to transfer of matter from one half-cell to the other owing to a concentration difference. These cells are called *concentration cells*. The concentration cells are of two kinds : (1) *Amalgam cells* and (2) *Electrolyte concentration cells*.

XIII.10. Amalgam Cells. In amalgam cells two like electrodes of different activities are dipped in the same solution of an electrolyte containing an ion of the electrode material. Thus if two amalgams of silver of different concentrations be in contact with a silver nitrate solution, as

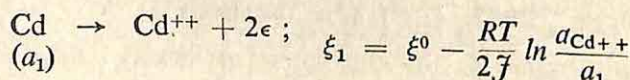


then it is an electrode concentration cell. The activities of silver in the two amalgams are different. Since in majority of cases metals are used as electrodes and to have them in different activities these are taken in the form of amalgams, hence the name amalgam cells.

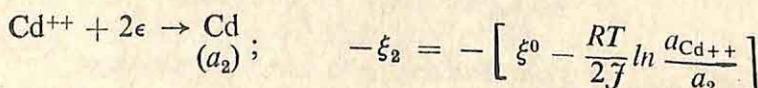
Consider the cadmium amalgam cell in which the anode amalgam has an activity a_1 for cadmium and the cathode amalgam has an activity a_2 for the same. The cell is



When current is drawn, the electrode process at the anode is dissolution of Cd *i.e.*, oxidation.



At the cathode reduction occurs, *i.e.*,

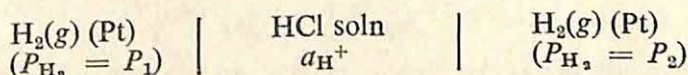


The net e.m.f. of the cell is

$$E = \xi_1 - \xi_2 = \frac{RT}{2f} \ln \frac{a_1}{a_2} \quad \dots \text{ (XIII.22)}$$

The net result is the transport of a gm-mol of Cd from the anode to the cathode. To have E as positive a_1 must be greater than a_2 , i.e., the amalgam with a higher concentration of Cd must act as anode.

Although not an amalgam, electrode-concentration cells with hydrogen electrodes at two different pressures with a HCl-solution can be easily obtained. The cell is



In the process of oxidation at the left electrode,

$$\xi_1 = -\frac{RT}{f} \ln \frac{a_{\text{H}^+}}{\sqrt{P_1}} \quad [\text{Reaction : } \frac{1}{2}\text{H}_2 \rightarrow \text{H}^+ + e]$$

For the process of reduction at the right electrode,

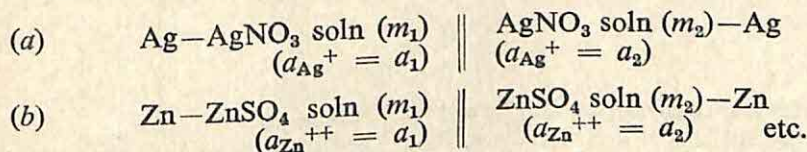
$$-\xi_2 = \frac{RT}{f} \ln \frac{\sqrt{P_2}}{a_{\text{H}^+}} \quad [\text{Reaction : } \text{H}^+ + e = \frac{1}{2}\text{H}_2]$$

$$\text{The e.m.f. of the cell, } E = \xi_1 + \xi_2 = -\frac{RT}{f} \ln \left(\frac{P_2}{P_1} \right)^{\frac{1}{2}} = -\frac{RT}{2f} \ln \frac{P_2}{P_1}$$

The e.m.f. depends only on the pressures of the gas at the two electrodes. For positive value of E , P_1 must be greater than P_2 . That is, the electrode where the gas pressure is larger will be the anode of the cell.

Since in these cells only one electrolyte is used. There is no liquid junction potential. So these are concentration cells without transference.

XIII.11. Electrolyte Concentration Cells. In this type of cells, the electrodes on the two sides are the same but they are dipped into solutions differing in the concentrations of the reversible ion ; such as,



Both the electrodes in such a cell would be of the same material but the potentials of the two electrodes will not be the same as the concentrations (and hence the activities) of the reversible ions in the two solutions are not the same.

In drawing current from such a cell the two electrodes will operate in opposition. If we take the AgNO_3 -concentration cell, at one electrode silver will be deposited while silver will be dissolved in the other and the process will continue until the activities in the two solutions become equal. Let us denote the activities of Ag^+ in the two solutions by a_1 and a_2 , such that $a_2 > a_1$. In the natural process of attaining equilibrium, silver will be deposited on the electrode in the more concentrated solution, where, therefore, the process is one of reduction. If ξ_1 and ξ_2 denote the oxidation potentials of the electrodes, then the net e.m.f. of the cell will be

$$E = \xi_1 - \xi_2 = \left(\xi_1^0 - \frac{RT}{nf} \ln a_1 \right) - \left(\xi_2^0 - \frac{RT}{nf} \ln a_2 \right)$$

Since, the same metal is used in both electrodes, $\xi_1^0 = \xi_2^0$

$$\text{Hence,} \quad E = \frac{RT}{nf} \ln \frac{a_2}{a_1} \quad \dots \text{ (XIII.23)}$$

Since $a_2 > a_1$, E is positive. Therefore, $\xi_1 > \xi_2$, i.e., oxidation is greater in the electrode in dilute solution. The current will flow in the external circuit from the electrode dipped in more concentrated solution.

When the molal concentrations and activity coefficients are denoted by the symbols m and γ , then,

$$\begin{aligned} E &= \frac{RT}{n\mathcal{F}} \ln \frac{m_2 \gamma_2}{m_1 \gamma_1} \\ &= \frac{RT}{n\mathcal{F}} \ln \frac{m_2}{m_1} + \frac{RT}{n\mathcal{F}} \ln \frac{\gamma_2}{\gamma_1} \quad \dots \text{(XIII.24)} \end{aligned}$$

The e.m.f. depends primarily on the concentration ratio of the two electrolytes, for which such cells are named concentration cells. Evidently larger is the value of $\frac{m_2}{m_1}$, greater will be the e.m.f. The liquid junction potential has been supposed to be eliminated and this result is valid for a concentration cell without transference.

XIII.12. Liquid Junction Potentials. When two solutions of different composition or concentration are brought together, a potential difference develops at the junction. This potential difference is called the liquid junction potential. The potential difference arises mainly due to the unequal rates of diffusion of the ions across the junction. (See Sec. XIII.9). Consider a cell of the type,



in which the solution of HCl in chamber II at the left has a concentration c_2 (activity a_2) and in contact with it is the solution of HCl in chamber I on the right, which has a concentration c_1 (activity a_1). Let us assume $c_1 > c_2$ and $a_1 > a_2$.

When we consider only the electrode-potentials and ignore the liquid-junction, the e.m.f. of this concentration cell will be given by, (equation XIII.23).

$$E = \frac{RT}{\mathcal{F}} \ln \frac{a_1}{a_2}$$

Let us now proceed to incorporate the liquid junction potential.

There will be diffusion of electrolytes from the solution of higher concentration to that of lower concentration. Because different ions have different mobilities, they tend to diffuse across the boundary at different speeds.

The ionic mobility (*i.e.*, velocity under unit potential gradient) of H^+ ions is higher than that of Cl^- ions. So H^+ ions will diffuse more rapidly from I to II. The dilute solution in chamber II will thus become positively charged with respect to the concentrated solution in chamber I. In consequence of this, the diffusion rate of Cl^- ions is enhanced and that of H^+ ions reduced until the two rates are equal across the electrical double layer produced at the junction. When the stationary state is thus attained, the potential difference between the two solutions at the boundary is the *liquid junction potential*. The potential of such a junction cannot be measured directly. It can be calculated in the following way.

Suppose now one faraday of electricity passes within the cell across the liquid junction. This will cause a transfer of t_+ gm-ions of H^+ ion from I to II and t_- gm-ions of Cl^- ion from II to I, where t_+ and t_- are the transference numbers of H^+ and Cl^- ions. This transfer process at the junction may be represented as :



The thermodynamic potential change of the process of transfer would be

$$\Delta G = -RT \ln K + RT \ln \frac{a_{\text{H}_\text{II}}^{t_+} a_{\text{Cl}_\text{I}}^{t_-}}{a_{\text{H}_\text{I}}^{t_+} a_{\text{Cl}_\text{II}}^{t_-}}$$

The value of the equilibrium constant K can be determined by making $a_{\text{H}^+}^{\text{I}} = a_{\text{H}^+}^{\text{II}} = 1$, and $a_{\text{Cl}^-}^{\text{I}} = a_{\text{Cl}^-}^{\text{II}} = 1$, when $K = 1$, i.e., $\ln K = 0$.

$$\therefore \Delta G = RT \ln \frac{a_{\text{H}^+}^{\text{II}} a_{\text{Cl}^-}^{\text{I}}}{a_{\text{H}^+}^{\text{I}} a_{\text{Cl}^-}^{\text{II}}} = RT \left[t_+ \ln \frac{a_{\text{H}^+}^{\text{II}}}{a_{\text{H}^+}^{\text{I}}} - t_- \ln \frac{a_{\text{Cl}^-}^{\text{II}}}{a_{\text{Cl}^-}^{\text{I}}} \right]$$

$$\begin{aligned} \text{Hence, } \Delta G &= RT \left[t_+ \ln \frac{a_{\text{H}^+}^{\text{II}}}{a_{\text{H}^+}^{\text{I}}} - (1-t_+) \ln \frac{a_{\text{Cl}^-}^{\text{II}}}{a_{\text{Cl}^-}^{\text{I}}} \right] \\ &= RT \left[t_+ \ln \frac{a_{\text{H}^+}^{\text{II}} \cdot a_{\text{Cl}^-}^{\text{I}}}{a_{\text{H}^+}^{\text{I}} \cdot a_{\text{Cl}^-}^{\text{II}}} - \ln \frac{a_{\text{Cl}^-}^{\text{II}}}{a_{\text{Cl}^-}^{\text{I}}} \right] \end{aligned}$$

If a_2 and a_1 represent the mean activities of the two HCl solutions, then $a_2^2 = a_{\text{H}^+}^{\text{II}} \cdot a_{\text{Cl}^-}^{\text{II}}$ and $a_1^2 = a_{\text{H}^+}^{\text{I}} \cdot a_{\text{Cl}^-}^{\text{I}}$. Further, the ratio of individual ionic activities may be assumed to be equal to the ratio of mean activities of the electrolyte, i.e., $a_{\text{Cl}^-}^{\text{II}}/a_{\text{Cl}^-}^{\text{I}} = a_2/a_1$.

Substituting these, we have

$$\begin{aligned} \Delta G &= RT \left[t_+ \ln \frac{a_2^2}{a_1^2} - \ln \frac{a_2}{a_1} \right] = (2t_+ - 1) RT \ln \frac{a_2}{a_1} \\ &= -(t_- - t_+) RT \ln \frac{a_2}{a_1} = -\frac{v-u}{v+u} RT \ln \frac{a_2}{a_1} \end{aligned}$$

where v and u are the mobilities of Cl^- and H^+ ions respectively.

If ξ_j be the liquid junction potential, then

$$\begin{aligned} \Delta G &= -n\mathcal{F}\xi_j = -\mathcal{F}\xi_j & (\text{Since } n = 1) \\ \xi_j &= \frac{v-u}{v+u} \cdot \frac{RT}{\mathcal{F}} \ln \frac{a_2}{a_1} & \dots (\text{XIII.25}) \end{aligned}$$

Since $v < u$ and $a_2 < a_1$, so ξ_j is positive. Hence, the dilute solution side of the junction in this case is positive, as assumed. This will therefore oppose the direction of the current.

The e.m.f. of this concentration cell without transference,

$$E = \frac{RT}{\mathcal{F}} \ln \frac{a_1}{a_2},$$

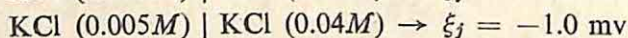
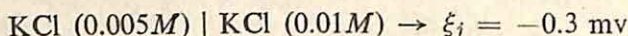
when only the single electrode potentials are considered and the liquid junction potential is ignored. The liquid junction potential is opposed to this. The net e.m.f. of the concentration cell with transference would be

$$\begin{aligned} E' &= E - \xi_j = \frac{RT}{\mathcal{F}} \ln \frac{a_1}{a_2} - \frac{v-u}{v+u} \frac{RT}{\mathcal{F}} \ln \frac{a_2}{a_1} \\ &= \frac{2v}{v+u} \cdot \frac{RT}{\mathcal{F}} \ln \frac{a_1}{a_2} \\ &= 2t_- \frac{RT}{\mathcal{F}} \ln \frac{a_1}{a_2} & \dots (\text{XIII.26}) \end{aligned}$$

The equation (XIII.25) is valid only for the junction of solutions of the same electrolyte with different concentrations and the electrolyte is a uni-univalent one.

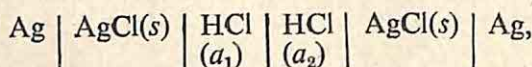
In case, $v = u$, i.e., if we choose an electrolyte in which the ionic mobilities of the cation and the anion are equal, the liquid junction potential will be nil. This explains the choice of KCl-bridge in eliminating liquid junction potential during experiments, for u_{K^+} is almost equal to v_{Cl^-} .

The ξ_j -values of KCl solutions are :



It is interesting to note that the e.m.f. depends on the transport number of the anion (t_-), although the electrodes are reversible with respect to the cation (H^+).

If we take a concentration cell with electrodes reversible with respect to anion such as,



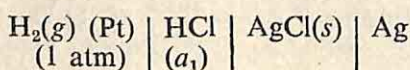
following the same procedure, the e.m.f. (E) would be

$$E = 2t_+ \cdot \frac{RT}{f} \ln \frac{a_1}{a_2}$$

The e.m.f. would thus depend in this case on the transport number of the cation.

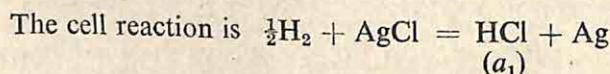
XIII.12a. Electrolyte Concentration Cells without Transference. It is sometimes possible to construct a concentration cell by combining two chemical cells in opposition in such a way that liquid junction potential is eliminated.

In the chemical cell,

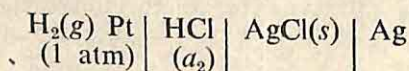


the e.m.f. is

$$E_1 = E^0 - \frac{RT}{f} \ln a_1 \quad \dots (A)$$

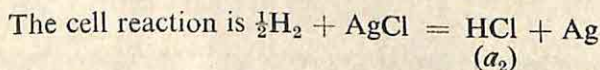


A second cell of the same electrodes with a different activity of HCl, such as

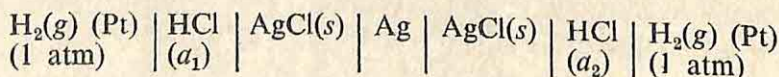


will have the e.m.f.

$$E_2 = E^0 - \frac{RT}{f} \ln a_2 \quad \dots (B)$$



The two cells may now be combined in opposition such that a cell of the following kind would occur.



The e.m.f. of the combination cell will be

$$\begin{aligned} E &= E_1 - E_2 = \left(E^0 - \frac{RT}{f} \ln a_1 \right) - \left(E^0 - \frac{RT}{f} \ln a_2 \right) \\ &= -\frac{RT}{f} \ln \frac{a_1}{a_2} = \frac{RT}{f} \ln \frac{a_2}{a_1} \quad \dots (\text{XIII.27}) \end{aligned}$$

(b) *Determination of Transport Number.* The e.m.f. of a concentration cell with transference, and without transference, are

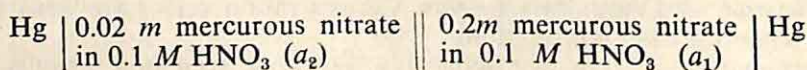
$$E_t = 2t_- \cdot \frac{RT}{f} \ln \frac{a_1}{a_2}; \quad E = \frac{RT}{f} \ln \frac{a_1}{a_2}$$

Hence

$$E_t/E = 2t_-$$

Thus the measurement of e.m.f. of two cells would provide the required answer.

(c) *Determination of Valence of an Ion.* The measurement of e.m.f. of concentration cell is also used in obtaining the valence of an ion with respect to which the electrodes are reversible. For example, the e.m.f. of the concentration cell,



is given by

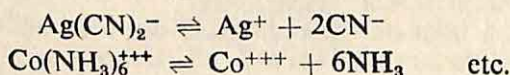
$$E = \frac{RT}{nf} \ln \frac{a_1}{a_2}$$

The solutions being dilute, the ratio $\frac{a_1}{a_2} \approx \frac{c_1}{c_2} \approx 10$, hence

$$E = (2.303) \frac{RT}{nf} = \frac{0.059}{n} \quad \text{at } 25^\circ\text{C.}$$

Since E is measured, the valence of mercurous ion (n) is known. This method has in effect been utilised earlier in section XIII.8, when each of the half-cells was balanced separately against a reference electrode.

(d) *Determination of the Composition of Complex Ions.* There exists an equilibrium in solution between the complex ion and the ions (or molecules) from which the former is produced, e.g.,

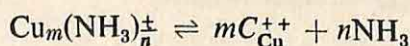


So, the the equilibrium constant, called instability constant, is

$$K_i = \frac{C_{\text{M}^+}^q \cdot C_{\text{A}^-}^r}{C_{\text{M}_q\text{A}_r}}, \quad \dots \text{ (XIII.30)}$$

the concentration terms are used in place of activities in order to simplify the treatment.

Bodlander (1901) used e.m.f. measurements in finding out the composition of complex ions. Let us illustrate the method with the example of cuprammonium ion. Take two solutions of copper ion in ammonia. The solutions will contain the complex ion $\text{Cu}_m(\text{NH}_3)_n^\pm$ ion in equilibrium with Cu^{++} ions and NH_3 molecules. Let C_{NH_3} and C'_{NH_3} be concentrations of ammonia in the two solutions in which copper ion concentration are C_{Cu} and C'_{Cu} and the complex ion concentration C_C and C'_C .



$$\text{Then,} \quad K_i = \frac{C_{\text{NH}_3}^n \cdot C_{\text{Cu}^{++}}^m}{C_C} = \frac{C'_{\text{NH}_3} \cdot C'_{\text{Cu}^{++}}}{C'_C}$$

or

$$\frac{C_{\text{Cu}^{++}}^m}{C_{\text{Cu}^{++}}'^m} = \frac{C_{\text{NH}_3}^n \cdot C_C}{C_{\text{NH}_3}' \cdot C'_C} \quad \dots \text{ (A)}$$

Next construct a concentration cell with the two solutions, excluding junction potential, with copper electrodes dipped in them. The e.m.f. (E) of the cell is also measured. We know,

$$E = \frac{RT}{2f} \ln \frac{C_{\text{Cu}^{++}}}{C'_{\text{Cu}^{++}}}$$

$$\text{Substituting (A), } E = \frac{RT}{2mf} \cdot \ln \frac{C_C \cdot C'_{\text{NH}_3}}{C'_C C_{\text{NH}_3}} \quad \dots (B)$$

If the concentration of ammonia used in the two solutions be equal and relatively much larger than those of copper ions $C_{\text{NH}_3} \approx C'_{\text{NH}_3}$, Then

$$E = \frac{RT}{2mf} \ln \frac{C_C}{C'_C}$$

When the complex ion is quite stable and ammonia is in excess, the whole of copper ion would practically be in the complex, so $\frac{C_C}{C'_C} = \frac{C_{\text{Cu}}}{C'_{\text{Cu}}}$ Hence the measured e.m.f.,

$$E = \frac{RT}{2mf} \ln \frac{C_{\text{Cu}^{++}}}{C'_{\text{Cu}^{++}}}$$

The concentration of copper ions being originally known and E experimentally observed, the number of copper ions (m) in the complex is evaluated.

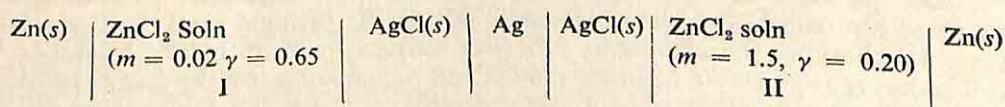
In the next set of experiments, the two solutions should contain the same total concentration of copper while ammonia should be present in large excess but at different concentrations. Again, the whole of copper ion taken would remain in the complex ion. Since $C_{\text{Cu}^{++}} = C'_{\text{Cu}^{++}}$, so $C_C = C'_C$ i.e., concentration of complex ions would be equal. By substitution of this in equation (B) above, the observed e.m.f. would be

$$E' = \frac{RT}{2mf} \ln \frac{C'_{\text{NH}_3}}{C_{\text{NH}_3}} = \frac{RT}{2mnf} \cdot \ln \frac{C'_{\text{NH}_3}}{C_{\text{NH}_3}}$$

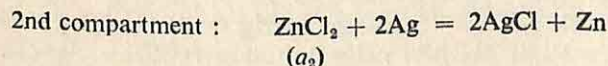
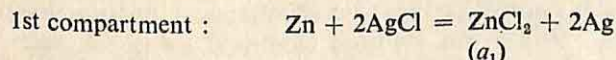
As m is already known, the value of n is easily obtained. The knowledge of m and n gives the composition of the complex ion. The method can be extended to the cases of other complex ions.

Some Calculations :

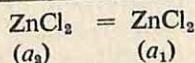
1. Calculate the e.m.f. of the cell,



This is a concentration cell without transference. The cell reactions are :



Hence



That is, with the passage of 2 faradays of electrical energy, 1 mole of ZnCl_2 is transferred from II to I.

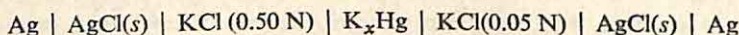
The e.m.f. of the cell is then

$$E = \frac{3RT}{2f} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1} = \frac{3RT}{2f} \ln \frac{a_2^{\frac{1}{3}}}{a_1^{\frac{1}{3}}} = \frac{RT}{2f} \ln \frac{a_2}{a_1} \quad (v = 3)$$

$$= \frac{RT}{2f} \times 2.303 \log \frac{m_2 \gamma_2}{m_1 \gamma_1}$$

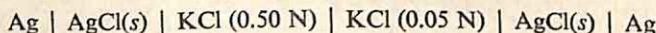
or
$$E = 0.028 \log \frac{1.5 \times 0.3}{0.02 \times 0.65} = 0.1386 \text{ volts.}$$

2. The concentration cell,



has an e.m.f. -0.10740 volts. Formulate the corresponding cell with transference, for which the e.m.f. is found to be -0.05357 volts. Find out the transport number of Cl^- ion.

The cell with transference is



Being reversible with respect to Cl^- ion, this cell has an e.m.f.

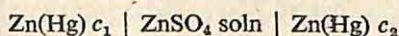
$$E_t = 2t_+ \frac{RT}{f} \ln \frac{a_1}{a_2}$$

But the e.m.f. of the given cell is
$$E = \frac{2RT}{f} \ln \frac{a_1}{a_2}$$

So,
$$t_+ = \frac{E_t}{E} = \frac{-0.05357}{-0.10740} = 0.498$$

hence
$$t_- = 1 - 0.498 = 0.502.$$

3. Calculate the e.m.f. of the amalgam concentration cell, at 60°C ,



When $c_1 = 6.08 \times 10^{-5}$ and $c_2 = 2.28 \times 10^{-3}$ gm-atoms per litre.

As arranged, $c_2 > c_1$, the cell will have a negative e.m.f., or

$$E = -\frac{RT}{2f} \ln \frac{c_2}{c_1} = -\frac{8.314 \times (273 + 60) \times 2.303}{2 \times 96500} \log \frac{2.28 \times 10^{-3}}{6.08 \times 10^{-5}} = -0.051 \text{ volts}$$

XIII.14. Cells in Commercial Use. Some galvanic cells are commonly used as sources for supply of electrical energy for different commercial purposes. These cells are of two categories—*primary cells* and *secondary cells*.

The primary cells are those in which the chemicals used up during supply of energy cannot be produced back by passing current into the exhausted cell from external source. The used up cell cannot be rejuvenated. Dry cells used in torches, radio receivers, hearing aids etc., are primary cells.

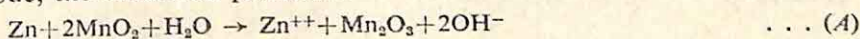
On the other hand, in the *secondary cells* or *storage cells* or *accumulators* as these are called, the chemicals used up can be brought back to the original state by charging the exhausted cell with current from an external source. The cell is thus reproduced in its original state and is again fit to supply energy as before. The process can be repeated over and over again. These cells can then be used for storage of electrical energy, hence the name.

The production of electrical energy at the cost of chemical energy inside is called "*discharging*" of the cell. When the external electrical energy is supplied into the cell to be transformed into chemical energy, the process is "*charging*" of the cell. In storage cells, these processes must be as nearly reversible as possible. Theoretically speaking, other reversible galvanic cells should also behave as storage cells through alternate charging and discharging. The Daniell cell or the Hydrogen-chlorine cell being reversible should function as typical storage cells. But such cells are not ideal from technical standpoint. The Daniell cell when charged will regenerate zinc but in a spongy form and the internal resistance is also high. The gas-cells though reversible are obviously unsuitable for commercial transport. Good accumulators are required to satisfy certain conditions : these should retain

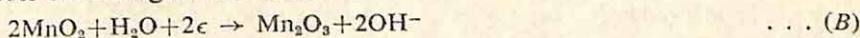
the stored electrical energy without any loss for a considerable period when not in use ; the resistance of an accumulator must be low and its construction simple. The principles involved in a few commercial cells are discussed here.

The Leclanche' or Dry Cell. It is a primary cell in which a zinc plate is the negative electrode and the positive electrode is a carbon rod. The zinc plate usually forms the outer covering of the cell. The electrolyte is a paste of MnO_2 , NH_4Cl and ZnCl_2 and the space between the central carbon electrode and the zinc plate is completely filled with the paste.

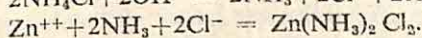
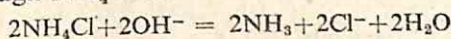
At the anode, the oxidation process is



and the reduction occurring at the cathode is

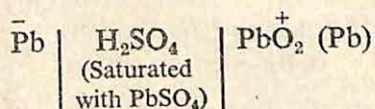


Subsequently, secondary chemical reactions occur which consume the OH^- and Zn^{++} through NH_4Cl as

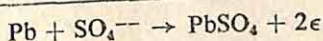
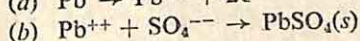
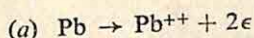


The result is that the exhausted dry cell cannot be brought back to the original state. The e.m.f. of the cell depends upon the reactions (A) and (B). The potential of the cell is about 1.5 volts.

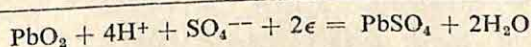
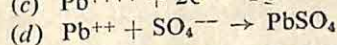
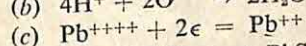
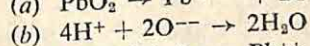
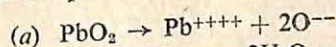
The Lead Accumulator or Acid Storage Cell. In this cell the negative electrode is lead and the positive electrode is lead with an adherent layer of PbO_2 on its surface. The electrolyte is H_2SO_4 (Sp. gr. 1.15). The cell is



(i) At the negative electrode, lead dissolves to form Pb^{++} ions, which then react with sulphate ions to be precipitated as sulphate. So,

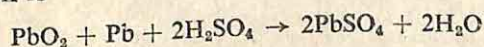


(ii) At the positive electrode, the reactions are expressed as

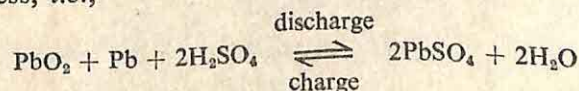


That is, the plumbic ion is reduced to Pb^{++} ions and ultimately lead sulphate is formed in the cathode as well.

In the process when the accumulator gives current *i.e.*, in discharging, the net cell reaction is



When the cell is discharged appreciably, *i.e.*, PbSO_4 formed at both electrodes, the cell is charged by passing a current from an external e.m.f. which reverses the chemical process, *i.e.*,



During charging Pb is deposited on the original anode and PbO_2 is formed on the cathode. H_2SO_4 is regenerated.

The anode potential would be

$$\xi_1 = \xi_{\text{Pb/Pb}^{++}}^0 - \frac{RT}{2f} \ln \frac{a_{\text{Pb}^{++}}}{a_{\text{Pb}}}, \quad \xi_{\text{Pb/Pb}^{++}}^0 = 0.12$$

and the cathode potential, (considering it as $\text{Pb}^{4+}/\text{Pb}^{2+}$ electrode)

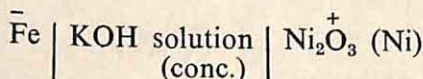
$$\xi_2 = \xi_{\text{Pb}^{++}/\text{Pb}^{4+}}^0 - \frac{RT}{2f} \ln \frac{a_{\text{Pb}^{4+}}}{a_{\text{Pb}^{++}}}, \quad \xi_{\text{Pb}^{2+}/\text{Pb}^{4+}}^0 = -1.74$$

Hence, the net e.m.f. of the cell is

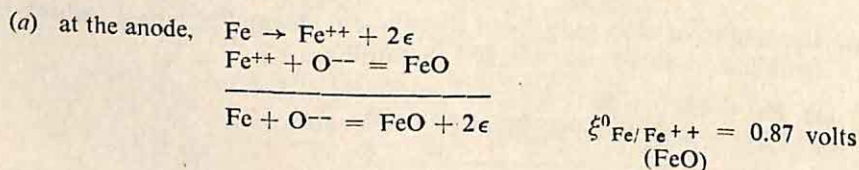
$$\begin{aligned} E &= \xi_1 + (-\xi_2) = \xi_{\text{Pb/Pb}^{++}}^0 - \xi_{\text{Pb}^{++}/\text{Pb}^{4+}}^0 + \frac{RT}{2f} \ln \frac{a_{\text{Pb}^{4+}}}{a_{\text{Pb}^{++}}^2} \\ &= 0.12 + 1.74 + \frac{RT}{2f} \ln \frac{a_{\text{Pb}^{4+}}}{a_{\text{Pb}^{++}}^2} = 1.86 + 0.029 \log \frac{a_{\text{Pb}^{4+}}}{a_{\text{Pb}^{++}}^2}. \end{aligned}$$

The activities of lead ions on the right-hand side depends upon the concentration of the H_2SO_4 used. The normal value of the e.m.f. of lead accumulator using H_2SO_4 of sp. gr. 1.15 is about 2.07 volts.

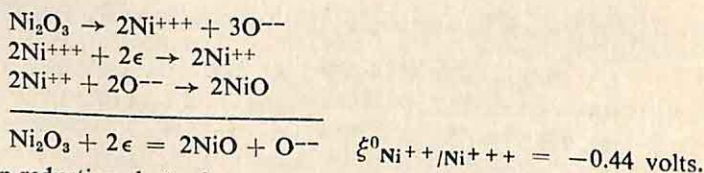
The Edison Accumulator or Alkali Storage Cell. In the Edison accumulator concentrated KOH solution is used as electrolyte, hence the name alkali storage cell. The anode is a sheet of iron and the cathode a nickel plate impregnated with Ni_2O_3 .



The half-cell reactions are :



(b) at the cathode,



This is really an oxidation-reduction electrode.

The net cell reaction is, $\text{Fe} + \text{Ni}_2\text{O}_3 \rightarrow \text{FeO} + 2\text{NiO}$. The opposite change takes place when the spent-up cell is charged. The oxides really exist in hydrated forms but these have been shown as oxides only to simplify the treatment.

The electrode potentials are,

$$\xi_1 = \xi_{\text{Fe/Fe}^{++}}^0 - \frac{RT}{2f} \ln a_{\text{Fe}^{++}}; \quad \xi_2 = \xi_{\text{Ni}^{++}/\text{Ni}^{+++}}^0 - \frac{RT}{f} \ln a_{\text{Ni}^{+++}/\text{Ni}^{++}}$$

$$\begin{aligned} \text{Hence } E &= \xi_1 + (-\xi_2) = \xi_{\text{Fe/Fe}^{++}}^0 - \xi_{\text{Ni}^{++}/\text{Ni}^{+++}}^0 + \frac{RT}{2f} \ln \frac{a_{\text{Ni}^{+++}}^2}{a_{\text{Ni}^{++}}^2 \times a_{\text{Fe}^{++}}} \\ &= 1.31 + 0.029 \log \frac{a_{\text{Ni}^{+++}}^2}{a_{\text{Ni}^{++}}^2 \times a_{\text{Fe}^{++}}}. \end{aligned}$$

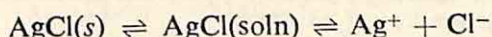
It is evident that the concentration of alkali remains undisturbed, the e.m.f. does not materially depend upon the alkali concentration. The usual e.m.f. is about 1.35 volts.

IONIC EQUILIBRIA

In the pages following, we shall discuss the equilibria of ions in solution in the study of which measurements of e.m.f. and of conductance are most helpful.

SOLUBILITY PRODUCT

XIII.15. Solubility Product. When a saturated solution of a salt, say AgCl, is in contact with the solid phase, there is the equilibrium,



The solid is in equilibrium with the ions in solution.

The thermodynamic potential change in the process of ionisation is given by

$$-\Delta G = \mu_{\text{Ag}^+} + \mu_{\text{Cl}^-} - \mu_{\text{AgCl}(s)}$$

where μ -terms are chemical potentials.

At equilibrium, at a given temperature (T), $\Delta G = 0$

$$\therefore \mu_{\text{AgCl}(s)} = \mu_{\text{Ag}^+} + \mu_{\text{Cl}^-}$$

i.e., $\mu_{\text{AgCl}(s)}^0 + RT \ln a_{\text{AgCl}(s)} = \mu_{\text{Ag}^+}^0 + RT \ln a_{\text{Ag}^+} + \mu_{\text{Cl}^-}^0 + RT \ln a_{\text{Cl}^-}$
(vide eqn. IV.121)

$$\text{or} \quad RT \ln \frac{a_{\text{Ag}^+} \cdot a_{\text{Cl}^-}}{a_{\text{AgCl}(s)}} = \mu_{\text{AgCl}(s)}^0 - \mu_{\text{Ag}^+}^0 - \mu_{\text{Cl}^-}^0 = z \text{ (constant)}$$

Since at a given temperature $a_{\text{AgCl}(s)}$ is a constant, we have

$$\ln (a_{\text{Ag}^+} \cdot a_{\text{Cl}^-}) = \frac{z}{RT}$$

$$\text{or} \quad a_{\text{Ag}^+} \cdot a_{\text{Cl}^-} = L_a \text{ (constant)} \quad \dots \text{ (XIII.31)}$$

L_a is called the *activity product* or *activity solubility product* for the salt at a given temperature.

Replacing activities with molar concentrations and corresponding activity coefficients,

$$L_a = C_{\text{Ag}^+} f_{\text{Ag}^+} \cdot C_{\text{Cl}^-} f_{\text{Cl}^-}$$

$$\text{or} \quad L_a = [C_{\text{Ag}^+} \cdot C_{\text{Cl}^-}] \cdot f_{\pm}^2 \quad \dots \text{ (XIII.32)}$$

If we apply this relation to saturated solutions of sparingly soluble salts, like AgCl, BaSO₄, HgS, etc. the concentration of ions in the solution will be very low, and hence activity coefficient $f_{\pm}$ will be practically unity. In such circumstances,

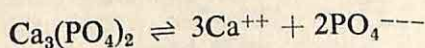
$$C_{\text{Ag}^+} \cdot C_{\text{Cl}^-} = L_s \text{ (say)} \quad \dots \text{ (XIII.33)}$$

where L_s is called the solubility product of the salt.

It means that the *product of the concentrations of the ions in the saturated solution of a sparingly soluble salt is constant (L_s) and is the solubility product.*

$$\text{Obviously,} \quad L_a = L_s \cdot f_{\pm}^2 \quad \dots \text{ (XIII.34)}$$

The relations given in (XIII.32, 33, 34) are valid for uni-univalent and other symmetrical electrolytes. If we take a salt like Ca₃(PO₄)₂ in saturated solution, the equilibrium is

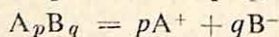


$$\therefore \quad L_a = a_{\text{Ca}^{++}}^3 \times a_{\text{PO}_4^{---}}^2$$

$$\text{and} \quad L_s = C_{\text{Ca}^{++}}^3 \times C_{\text{PO}_4^{---}}^2$$

$$\text{so that} \quad L_a = L_s \times f_{\pm}^5$$

Generally speaking for a salt A_pB_q ,



$$\therefore L_a = C_A^p \cdot f_+^p \times C_B^q \cdot f_-^q$$

$$= L_s \times f_{\pm}^v \quad \text{where } v = p+q \quad \dots \text{ (XIII.35)}$$

For a given salt at a fixed temperature, the value of the thermodynamic activity product L_a is unchangeable. The solubility product L_s will be constant in ideal conditions only if $f_{\pm}$ is unity. In that case, since $f_{\pm} = 1$, $L_a = L_s$. For ordinary work dealing with very sparingly soluble salts, the solutions are so dilute that $f_{\pm}$ is regarded as unity, hence L_s is a constant.

XIII.16. Solubility Product and Solubility. Suppose S is the solubility of the sparingly soluble salt, $AgCl$, in pure water expressed in gm-moles per litre. Since the solution is very dilute even when saturated, the salt is assumed completely dissociated and the concentrations of the ions are

$$C_{Ag^+} = S, C_{Cl^-} = S$$

$$\therefore \text{the solubility product, } L_s = S^2 \quad \dots \text{ (XIII.3.6)}$$

So, an estimation of solubility enables one to determine the solubility product.

Similarly, for the solubility of $Mg(OH)_2$, we have

$$C_{Mg^{++}} = S, C_{OH^-} = 2S$$

$$\therefore L_s = C_{Mg^{++}} \cdot C_{OH^-}^2 = S \cdot (2S)^2 = 4S^3$$

In general, if S be the solubility of a salt A_pB_q in pure water, which is sparingly soluble, we have, $C_{A^+} = pS$, $C_{B^-} = qS$ assuming complete dissociation and $f_{\pm} = 1$, Then

$$\left. \begin{aligned} L_s &= C_A^p \times C_B^q = (pS)^p \cdot (qS)^q = S^{p+q} (p^p q^q) \\ \text{or } L_s &= S^v \cdot (p^p q^q), \text{ where } v = p+q \\ \text{or } S &= \left(\frac{L_s}{p^p q^q} \right)^{\frac{1}{v}} \end{aligned} \right\} \quad \dots \text{ (XIII.37)}$$

This is the relation between solubility and solubility product ; for $AgCl$, $p = 1$, $q = 1$, $\therefore S = \sqrt{L_s}$

This means that at a given temperature the solubility of a salt is constant.

Two facts were however recognised early :

(i) The solubility of a sparingly soluble salt is greatly influenced by the presence of other salts in solution having no common ion with the saturating salt. Hence L_s will vary when other salts are present in the solution.

(ii) The product $L_s (= C_+ \cdot C_-)$ also does not remain constant when either C_+ or C_- is altered by addition of a compound containing one of these ions.

These are explained from equation XIII.35. The presence of increased concentration of inert salts increases the ionic strength (i) of the solution. Following Debye-Hückel limiting law, the increased ionic strength reduces the activity coefficient ($f_{\pm}$) of the saturating salt. Hence in order to maintain the constancy of

L_a , L_s must increase, i.e., solubility shall increase. "Solubility product" may vary but the activity product remains constant.

When a common ion is present, say, $AgCl$ is added to a KCl solution, the activity (or conc.) of Cl^- ion is large. The activity of Ag^+ ion should then diminish in order to maintain the constant value of L_a . In other words, the solubility of $AgCl$ must diminish.

Now $L_a = C_{Ag^+} \cdot C_{Cl^-} \cdot f_{\pm}$. But when the conc. of Cl^- ion already present is very large, the ionic strength increases considerably, so that $f_{\pm}$ for $AgCl$ would diminish

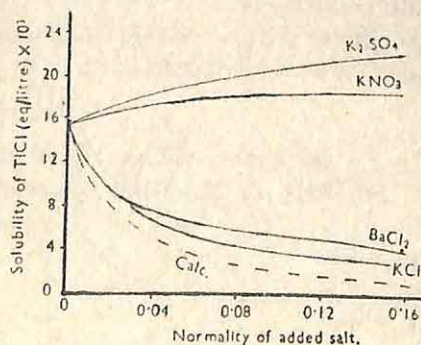


FIG. XIII.10 Effect of different salts on the solubility of $TiCl$

to a large extent. A point may be reached when C_{Ag^+} will tend to increase inspite of increase in C_{Cl^-} in order to compensate for the large decrease in $f_{\pm}$, remembering that L_a must be constant. The effect of the presence of inert salts and of common ions on the solubility is shown in Fig. XIII.10.

It is easily seen that if to a saturated solution of a sparingly soluble salt is added a compound containing a common ion the former will be thrown out of solution. If S be the solubility of $AgCl$ in pure water and suppose x gm-eqv. of KCl be added to a litre of the saturated solution. If S' be the solubility of $AgCl$ now, then, assuming KCl to be completely dissociated and $f_{\pm} = 1$,

$$\begin{aligned} L_s &= C_{Ag^+} \cdot C_{Cl^-} = S' (S' + x) \\ \text{But } L_s &= S^2; \text{ or } S' (S' + x) = S^2 \\ \text{i.e., } S' &= -\frac{x}{2} + \sqrt{\frac{x^2}{4} + S^2} = -\frac{x}{2} + \sqrt{\frac{x^2}{4} + L_s} \end{aligned}$$

The new solubility can thus be predicted.

A more rigorous calculation will be as follows.

$$\text{In pure water, } L_a = S^2 f_{\pm}^2$$

$$\text{and in KCl Solution, } L_a = (S') (S' + x) f_{\pm}'^2$$

$$\text{or } S' (S' + x) f_{\pm}'^2 = S^2 f_{\pm}^2$$

$$\text{whence } S' = -\frac{x}{2} + \sqrt{\frac{x^2}{4} + \left(S \cdot \frac{f_{\pm}}{f_{\pm}'}\right)^2}$$

Problem. Calculate the solubility product of silver chromate if its solubility be 2.5×10^{-2} gms per litre.

Also find out its solubility in $0.001 M$ potassium chromate solution. The activity coefficients may be taken as unity.

$$(a) \text{ Solubility of } Ag_2CrO_4 = \frac{2.5 \times 10^{-2}}{332} = 7.5 \times 10^{-5} \text{ moles/litre. (mol. wt. = 332)}$$

Assuming complete dissociation,

$$C_{Ag^+} = 2 \times 7.5 \times 10^{-5}$$

$$C_{CrO_4^{2-}} = 7.5 \times 10^{-5}$$

$$\text{The solubility product, } L_s = C_{Ag^+}^2 \cdot C_{CrO_4^{2-}} = (2 \times 7.5 \times 10^{-5})^2 (7.5 \times 10^{-5}) = 1.7 \times 10^{-12}$$

(b) The conc. of Ag^+ in saturated solution, in presence of pot chromate,

$$C_{Ag^+} = \left(\frac{L_s}{C_{CrO_4^{2-}}} \right)^{\frac{1}{2}} = \left(\frac{1.7 \times 10^{-12}}{1 \times 10^{-3}} \right)^{\frac{1}{2}} = 4.1 \times 10^{-5} \text{ moles/litre.}$$

Hence the solubility is 2.05×10^{-5} moles/litre.

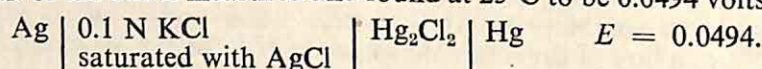
The decrease in solubility by common ion effect is of considerable importance in gravimetric analysis. Suppose silver is precipitated from a solution by potassium chromate. If exactly equivalent amount of chromate be added, the amount of silver that would remain in solution (see problem above) is 1.5×10^{-4} moles/litre. But if we use excess potassium chromate until its conc. is $0.001 M$, the loss will be reduced to 4.1×10^{-5} moles/litre. That is why the precipitant is to be added in excess. But too much excess is to be avoided; for in that case, the solubility of Ag_2CrO_4 may actually rise due to abnormal decrease in $f_{\pm}$.

When the addition of a common ion or an inert salt leads to a considerable increase in the solubility of a salt it may be reasonably concluded that a complex ion has been formed. This happens when say NH_4Cl is added to saturated $AgCl$ solution or KI solution is added to HgI_2 solution, etc.

XIII.17. Determination of Solubility Product. The solubility product of sparingly soluble salts is determined either from conductivity results or from measurement of e.m.f. of suitable cells.

In chapter XII [section 15(v), equation XII.38], we have seen how the solubility (S) of a sparingly soluble salt is determined from measurement of the conductance of its saturated solution in pure water. From a knowledge of the solubility S , the solubility product L_s is immediately known with equation (XIII.37). If it is a 1-1 electrolyte, then $L_s = S^2$, as in $AgCl$.

To illustrate the electrometric method for the determination of solubility product (L_s), we may again take the case of AgCl. In a solution of 0.1 *M* KCl ($f_{\pm} = 0.77$) is added a few drops of AgNO₃, so that the solution is saturated with AgCl, and a silver wire is inserted in the solution. This can serve as a silver electrode, Ag/Ag⁺. This electrode is coupled with a 0.1 *N* calomel electrode. The e.m.f. of the cell is measured and found at 25°C to be 0.0494 volts.



The e.m.f., $E = \xi_{\text{Ag}} - \xi_{\text{calomel}}$

or $0.0494 = \xi_{\text{Ag}} + 0.3338,$

whence, $\xi_{\text{Ag}} = -0.2844$ volts.

But $\xi_{\text{Ag}} = \xi_{\text{Ag}}^{\circ} - 0.059 \log a_{\text{Ag}^+}$, where $\xi_{\text{Ag}}^{\circ} = -0.799$

or $\log a_{\text{Ag}^+} = -\frac{0.799 - 0.2844}{0.059}$

whence $a_{\text{Ag}^+} = 2 \times 10^{-9}$

The activity of Cl⁻ ions in the solution is $0.1 \times 0.77 = 0.077$.

Hence, the activity product, $L_a = a_{\text{Ag}^+} \times a_{\text{Cl}^-}$

$$= 2 \times 10^{-9} \times 0.77 = 1.54 \times 10^{-10}$$

An alternative method would be to evaluate L_a from standard electrode potentials.

Since $\text{AgCl}(s) \rightarrow \text{Ag}^+ + \text{Cl}^-$; $K = a_{\text{Ag}^+} \times a_{\text{Cl}^-} = L_a$

If we imagine two single electrodes as

(anode) $\text{Ag}(s) \rightarrow \text{Ag}^+ + e$ $\xi_{\text{Ag}}^{\circ} = -0.7991$

and (cathode) $\text{AgCl}(s) + e \rightarrow \text{Ag}(s) + \text{Cl}^-$ $\xi_{\text{Ag-AgCl}}^{\circ} = -0.2223$

coupled, we have

$$\begin{aligned} E^{\circ} &= \xi_{\text{Ag}}^{\circ} - \xi_{\text{Ag-AgCl}}^{\circ} \\ &= -0.7991 + 0.2223 = -0.5768. \end{aligned}$$

Now $\log K = \frac{E^{\circ}}{0.059}$ at 25°C

i.e., $\log L_a = \frac{E^{\circ}}{0.059} = -\frac{0.5768}{0.059}$, whence $L_a = 1.6 \times 10^{-10}$

In the table appended below are given the solubility products of some common sparingly soluble compounds and salts at room temperature.

Substance	L_s	Substance	L_s
AgCl	1.5×10^{-10}	Fe(OH) ₃	1×10^{-38}
AgBr	7.7×10^{-13}	Al(OH) ₃	1×10^{-33}
AgI	0.9×10^{-16}	Cr(OH) ₃	1×10^{-30}
Ag ₂ CrO ₄	2.5×10^{-12}	Zn(OH) ₂	1×10^{-17}
BaSO ₄	9.2×10^{-11}	Co(OH) ₂	2×10^{-16}
CaSO ₄	2.3×10^{-4}	Ni(OH) ₂	1×10^{-14}
SrSO ₄	2.8×10^{-7}	Mg(OH) ₂	6×10^{-12}
PbCl ₂	2.4×10^{-4}	HgS	3×10^{-54}
PbBr ₂	7.9×10^{-5}	CuS	3×10^{-42}
PbI ₂	8.7×10^{-9}	CdS	4×10^{-29}
CaCO ₃	4.8×10^{-9}	PbS	4×10^{-28}
CaOx	2.6×10^{-9}	CoS	2×10^{-27}
CaF ₂	3.2×10^{-11}	ZnS	1×10^{-23}
CuCl	1×10^{-6}	NiS	1.4×10^{-24}
CuBr	1.6×10^{-11}	MnS	2×10^{-15}
CuI	5×10^{-12}		

XIII.18. Application of Solubility Measurements : (a) *Determination of Activity Coefficients.* The mean activity coefficient of a slightly soluble salt can be evaluated from the study of its solubilities in solutions of different ionic strength. We know, the activity product for a simple uni-univalent salt,

$$L_a = L_s f_{\pm}^2 = S^2 f_{\pm}^2$$

where $f_{\pm}$ is the mean activity coefficient, and S is its solubility in pure water. For convenience of writing the suffix $\pm$ is dropped, so $L_a = S^2 f^2$

$$\text{i.e.,} \quad f = \frac{\sqrt{L_a}}{S} \quad \dots \text{(XIII.38)}$$

$$\text{or} \quad \log S = \frac{1}{2} \log L_a - \log f \quad \dots \text{(XIII.39)}$$

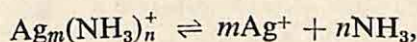
If S' be the solubility in any solution of ionic strength (i) where the mean activity coefficient of this salt is f' , then

$$\log S' = \frac{1}{2} \log L_a - \log f' \quad \dots \text{(XIII.40)}$$

In practice, the solubility of the given sparingly soluble salt is measured in very dilute solutions of different concentrations of added electrolytes. The observed solubilities or rather their logarithms ($\log S'$) are plotted against $\sqrt{i}$. The relation is a linear one, and when extrapolated, the value of solubility S_0 at $i = 0$ is known. That is S_0 is the solubility when $f = 1$. Substituting this S_0 in equation XIII.39, $\frac{1}{2} \log L_a$ is known.

L_a being thus known, the mean activity coefficient (f') of the salt at any other solution where solubility is S' is obtained from equation (XIII.40).

(b) *Determination of the Composition of a Complex Ion.* The composition of a complex ion can also be determined from a study of solubilities [cf. Sec. XIII.13d)]. Let us consider the silver ammonia complex ion and let us suppose its formula would be $\text{Ag}_m(\text{NH}_3)_n^+$; m and n are to be ascertained. Now,



$$\text{The instability constant,} \quad K_i = \frac{C_{\text{Ag}^+}^m \cdot C_{\text{NH}_3}^n}{C}$$

where C is the concentration of the complex.

Now suppose a solution of ammonia is saturated with AgCl . If L_s be the solubility product of silver chloride, then $C_{\text{Ag}^+} \times C_{\text{Cl}^-} = L_s$, or $C_{\text{Ag}^+} = L_s / C_{\text{Cl}^-}$.

$$\text{By substitution,} \quad K_i = \frac{L_s^m \times C_{\text{NH}_3}^n}{C_{\text{Cl}^-}^m \times C}$$

When the concentration of ammonia is large, practically the whole of Ag^+ will be in the complex. The concentration of chloride ion, (the same as the total quantity of Ag) is equal to the concentration of the complex, i.e., $C_{\text{Cl}^-} = C$.

$$\text{Hence} \quad K_i = \frac{L_s^m \times C_{\text{NH}_3}^n}{C^{m+1}}, \quad \text{or} \quad \frac{C_{\text{NH}_3}^n}{C^{m+1}} = \text{constant}$$

By making a large number of measurement of solubility of AgCl in different but excess concentrations of ammonia, the ratio $n/(m+1)$ may be determined.

In the next set of experiments, the solubility of silver chloride in a definite fixed concentration of ammonia but containing some known excess chloride ions

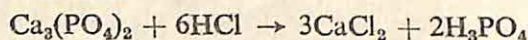
$$\text{is determined. In these cases,} \quad \frac{C_{\text{NH}_3}^n}{C_{\text{Cl}^-}^m \times C} = \text{constant.}$$

If total amount of silver i.e., conc. (C) is measured in different values of C_{Cl^-} , m will be easily determined.

Thus we can find out the value of both m and n , and the composition as well as the instability constant of the complex ion will be known.

XIII.19. Solubility Product and Analysis. The routine analytical scheme of inorganic samples is based on the operation of discriminatory dissolution and precipitation of the components of a mixture with the help of suitable reagents. These are all governed by the principle of solubility product.

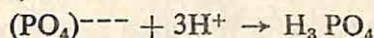
(a) *Solubility of Sparingly Soluble Salts of Weak Acids in Strong Acids.* There are many salts of weak acids, such as $\text{Ca}_3(\text{PO}_4)_2$, which are insoluble in water but are taken into solution with HCl .



In a saturated solution in water,

$$C_{\text{Ca}^{++}}^3 \times C_{\text{PO}_4^{---}}^2 = L_s$$

the solubility product is low and hence solubility is quite small. Addition of a strong acid, i.e., H^+ ions, reduces the phosphate ion concentration by forming undissociated phosphoric acid, as



The decrease in the concentration of PO_4^{+++} ions enables more calcium phosphate to go into solution to maintain the constancy of L_s . The addition of Cl^- ions along with H^+ ions do not affect, for CaCl_2 salt is highly soluble and practically fully ionised.

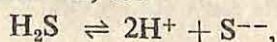
(b) *Precipitation from a Solution.* This indeed is the most important operation in analysis to separate out a component. The solubility product is the limiting value of the product of ionic concentrations $(C_+)^m \cdot (C_-)^n$ in the saturated state when solid phase is in equilibrium with the ions in solution. When the experimental conditions are arbitrarily so manipulated that the ionic concentration product exceeds the solubility product, the law demands that some ions must be removed. This is achieved by the system with the formation of solid phase, which is the precipitate. Thus to a barium nitrate solution if ammonium sulphate is added, the ionic concentration product $C_{\text{Ba}^{++}} \cdot C_{\text{SO}_4^{--}}$ almost immediately exceeds L_{BaSO_4} , which is very low (9.2×10^{-11}). Hence, the ions combine together to form the insoluble barium sulphate to be precipitated. The sulphate ions are therefore good precipitating agents for Ba^{++} . This is the story of other precipitations usually met with in the analytical scheme.

(c) *Precipitation of Sulphides.* It is common knowledge that basic radicals like those of Hg, Cu, Pb etc. are precipitated as sulphides in acid solution in Group II and those of Ni, Mn etc. are precipitated in alkaline media in Group IIIb. It may be remembered that the sulphides of the former category (Hg, Cu, etc.) have very low solubility products compared to those of the later category (Zn, Mn, Ni etc.).

Sulphides	L_s	Sulphides	L_s
HgS	3×10^{-54}	MnS	2×10^{-15}
CuS	3×10^{-42}	NiS	1.4×10^{-24}
PbS	4×10^{-28}	ZnS	1×10^{-23}

When H_2S is passed into solutions containing these radicals there arises the question of equilibrium between metal ions and the sulphide ions. As soon as the ionic concentration product exceeds the corresponding solubility product, the sulphide is precipitated.

It must be realised that the concentration of sulphide ion depends on the H^+ ion concentration in the solution, for



$$\text{i.e.,} \quad K_{\text{H}_2\text{S}} = \frac{C_{\text{H}^+}^2 \times C_{\text{S}^{--}}}{C_{\text{H}_2\text{S}}}$$

$$\text{or} \quad C_{\text{S}^{--}} = \frac{K_{\text{H}_2\text{S}} \times C_{\text{H}_2\text{S}}}{C_{\text{H}^+}^2}$$

where C_{H_2S} may be taken as the solubility of H_2S in water, which is about $M/10$ i.e., 10^{-1} . The concentration of sulphide ion is inversely proportional to the square of the H^+ ion concentration. So in acid solutions $C_{S^{--}}$ will be low and only those sulphides whose solubility product is very low shall be precipitated.

The magnitude of $K_{H_2S} = 1 \times 10^{-22}$

$$\therefore C_{S^{--}} = \frac{1 \times 10^{-22} \times 10^{-1}}{C_{H^+}^2} = \frac{1 \times 10^{-23}}{C_{H^+}^2}.$$

Suppose in a normal hydrochloric acid solution we have Cu^{++} and Mn^{++} ions present whose approximate concentrations are $M/10$. Then in this solution

if H_2S is passed, the concentration of sulphide ions, $C_{S^{--}} = \frac{1 \times 10^{-23}}{1^2} = 1 \times 10^{-23}$.

Then, the ionic product of Cu^{++} and S^{--} ions $= (1 \times 10^{-1})(1 \times 10^{-23}) = 1 \times 10^{-24}$, which is much larger than L_{CuS} and hence CuS will be precipitated in acid solution. But this value is much smaller than L_{MnS} and hence MnS will not be precipitated.

In alkaline solution, say with $C_{H^+} = 10^{-8}$, the sulphide ion concentration is $C_{S^{--}} = \frac{1 \times 10^{-23}}{10^{-16}} = 1 \times 10^{-7}$.

$\therefore$ ionic product $C_{Mn^{++}} \times C_{S^{--}} = (1 \times 10^{-1})(1 \times 10^{-7}) = 1 \times 10^{-8}$. Since this exceeds L_{MnS} , in alkaline medium manganese sulphide shall be precipitated.

The precipitation of Fe , Al , etc. as hydroxides, is also explained in the same way.

(d) *Use of K_2CrO_4 as Indicator.* In the estimation of a chloride by titration with silver nitrate solution, K_2CrO_4 solution is added to act as an indicator. Advantage is taken of the difference in the solubility products of silver chloride and silver chromate.

$$L_{AgCl} = C_{Ag^+} \cdot C_{Cl^-} = 1 \times 10^{-10}$$

$$L_{Ag_2CrO_4} = C_{Ag^+}^2 \cdot C_{CrO_4^{--}} = 2.5 \times 10^{-12}.$$

In titration, say a $\frac{N}{10}$ $NaCl$ solution with a $\frac{N}{10}$ $AgNO_3$ solution, potassium chromate is added such that its strength is approximately $M/100$. That is, at the beginning $C_{Cl^-} = 10^{-1}$, $C_{CrO_4^{--}} = 10^{-2}$.

When initially just a little $AgNO_3$ solution is added, say $C_{Ag^+} = 10^{-10}$ then ionic products will be,

$$C_{Ag^+} \cdot C_{Cl^-} = 10^{-10} \times 10^{-1} = 10^{-11}; \quad C_{Ag^+}^2 \cdot C_{CrO_4^{--}} = (10^{-10})^2 \times 10^{-2} = 10^{-22}.$$

These quantities are less than the solubility products of both and hence no ppt. will come out.

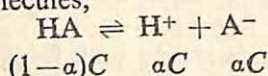
On further addition of $AgNO_3$, say $C_{Ag^+} = 10^{-8}$, we have $C_{Ag^+} \cdot C_{Cl^-} = 10^{-9}$, $C_{Ag^+}^2 \cdot C_{CrO_4^{--}} = 10^{-18}$. It is evident $AgCl$ will be precipitated but not Ag_2CrO_4 .

When precipitation of silver chloride is just complete, the conc. of $Ag^+ = 10^{-5}$. Therefore, $C_{Ag^+}^2 \cdot C_{CrO_4^{--}} = 10^{-12}$. On addition of just a little more $AgNO_3$ the conc. of Ag^+ will be large enough to cause ionic product $C_{Ag^+}^2 \cdot C_{CrO_4^{--}}$ exceed $L_{Ag_2CrO_4}$ ($= 2.5 \times 10^{-12}$) and hence Ag_2CrO_4 will begin to precipitate with its typical colour and the end point is known. Sufficient potassium chromate is to be used as indicator so as to produce enough silver chromate to saturate the solution and be precipitated.

ACIDS AND BASES

XIII.20. Dissociation Constant of Weak Acids. The strong acids and bases are completely ionised in solution and as such the law of mass action cannot be usefully applied to these. But in the case of weak acids and weak bases, the equilibrium constant principle is most aptly applicable.

In a solution of a weak acid, say HA, there is an equilibrium between the ions and the undissociated molecules,



The dissociation constant of the acid should be, in terms of activities,

$$K_a = \frac{a_{\text{H}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}} \quad \dots \text{(XIII.41)}$$

Expressing the activities in terms of concentrations and activity coefficients,

$$K_a = \frac{C_{\text{H}^+} \cdot f_{\text{H}^+} \times C_{\text{A}^-} \cdot f_{\text{A}^-}}{C_{\text{HA}} \cdot f_{\text{HA}}} = \frac{C_{\text{H}^+} \cdot C_{\text{A}^-}}{C_{\text{HA}}} \cdot \frac{f_{\text{H}^+} \cdot f_{\text{A}^-}}{f_{\text{HA}}} \quad \dots \text{(XIII.42)}$$

We know, from equation (XII.34), $\frac{C_{\text{H}^+} \cdot C_{\text{A}^-}}{C_{\text{HA}}} = K'_a$

i.e., the dissociation constant in terms of concentrations.

$$\text{Hence,} \quad K_a = K'_a \cdot \frac{f_{\text{H}^+} \cdot f_{\text{A}^-}}{f_{\text{HA}}}$$

But $f_{\text{H}^+} \cdot f_{\text{A}^-} = f_{\pm}^2$, the mean ionic activity coefficient squared, and in solutions of the electrolyte of ordinary concentration f_{HA} , the activity coefficient of unionised acid may be taken as unity. That is,

$$K_a = K'_a \cdot f_{\pm}^2 \quad \dots \text{(XIII.43)}$$

$$\text{Taking logarithms,} \quad \log K_a = \log K'_a + 2 \log f_{\pm} \quad \dots \text{(XIII.44)}$$

From the Debye-Hückel limiting law, we know,

$$\log f_{\pm} = -0.509 \, z_+ z_- \sqrt{i}$$

In a uni-univalent weak acid, like acetic acid, then

$$\log f_{\pm} = -0.509 \sqrt{aC}$$

where a is the degree of dissociation of a solution of concentration (C) of the acid. Substituting in (XIII.44),

$$\log K'_a = \log K_a + 1.018 \sqrt{aC} \quad \dots \text{(XIII.45)}$$

In section XII.15 (ii), it has been shown that K'_a can easily be determined from conductance measurement. Now, if K'_a is evaluated from conductance measurements at several low dilutions and the same be plotted against $(aC)^{\frac{1}{2}}$, a linear graph is obtained. Extrapolation of this line to $aC = 0$, will give $\log K_a$ and, hence K_a , the true dissociation constant (Fig. XIII.11).

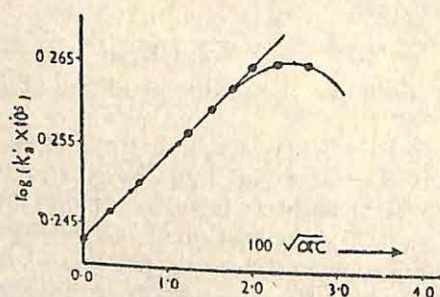


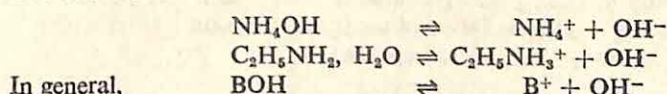
FIG. XIII.11 The variation of dissociation constant (K'_a) for acetic acid

The difference between K_a and K'_a is quite small, especially at low concentrations, and for many purposes, the easily determined dissociation constant K'_a is used without any appreciable error. A few of the values are given below :

TABLE : THE DISSOCIATION CONSTANTS OF ACETIC ACID AT 25°C

C	$K'_a \times 10^5$	$K_a \times 10^5$	C	$K'_a \times 10^5$	$K_a \times 10^5$
1.11×10^{-4}	1.78	1.75	2×10^{-2}	1.84	1.74
1.03×10^{-3}	1.80	1.75	5×10^{-2}	1.85	1.72
2.41×10^{-3}	1.81	1.75	9.84×10^{-3}	1.83	1.75

Dissociation Constant of Weak Bases. The dissociation of weak bases, like ammonium hydroxide, ethylamine, aniline etc. are also treated in the same way as that for weak acids.

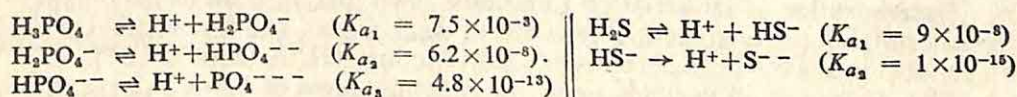


The equilibrium or dissociation constant of the base would be,

$$K_b = \frac{a_{\text{B}^+} \times a_{\text{OH}^-}}{a_{\text{BOH}}} = \frac{c_{\text{B}^+} \cdot c_{\text{OH}^-}}{c_{\text{BOH}}} \cdot \frac{f_{\text{B}^+} \cdot f_{\text{OH}^-}}{f_{\text{BOH}}} = K'_b \cdot f_{\pm}^2 \quad \dots \text{(XIII.46)}$$

In extremely dilute solutions $f_{\pm}$ tends to unity, so that $K_b = K'_b$. The true value of K_b is ascertained by the extrapolation method as in the case of weak acids (Fig. XIII.11).

Polybasic acids. The polybasic acids have more than one ionisable hydrogen and these ionise in successive stages. The degrees of ionisation at different stages are different and the dissociation constants for successive dissociation are also different. For example :



From the dissociation constants it is easy to find out the concentration of ions present in solution ; say for concentration H_2PO_4^- ion, $C_{\text{H}_2\text{PO}_4^-} \approx aC = \sqrt{k_1 C}$. It can be shown that in a $M/50$ phosphoric acid solution,

$$C_{\text{H}_2\text{PO}_4^-} = 0.01, C_{\text{HPO}_4^{--}} = 6 \times 10^{-8}, C_{\text{PO}_4^{---}} = 3 \times 10^{-18}$$

approximately. That is, even in a moderately dilute phosphoric acid solution, the concentration of PO_4^{---} ions is quite small.

Even with strong acids, like sulphuric acid, the first dissociation is practically complete. But in the second stage, i.e., $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{--}$, it behaves as a comparatively weak acid having a dissociation constant value of 1×10^{-2} at 25°C .

Common Ion Effect. It is easy to see that the presence of an ion common with one of those produced by dissociation will depress the degree of dissociation in order to maintain the constancy of K_a . Thus, in the case of acetic acid,

$$K'_a = \frac{C_{\text{H}^+} \times C_{\text{Ac}^-}}{C_{\text{HAc}}} ; \text{ if the solution already contains } \text{Ac}^- \text{ ion, to maintain } K'_a$$

constant, C_{H^+} must diminish ; i.e., dissociation would be less.

Example 1. A saturated solution of H_2S in water is $0.1 M$ at 25°C . The first and second dissociation constants are 9×10^{-8} and 1×10^{-15} respectively. Calculate the concentrations of S^{--} and HS^- ions.

Also find out the sulphide ion concentration in a $0.25 M \text{HCl}$.

$$C_{\text{H}^+} \cdot C_{\text{HS}^-} / C_{\text{H}_2\text{S}} = 9 \times 10^{-8} \quad \dots (a)$$

$$C_{\text{H}^+} \cdot C_{\text{S}^{--}} / C_{\text{HS}^-} = 1 \times 10^{-15} \quad \dots (b)$$

The value of K_2 , the second dissociation constant is very low and hence the concentration of S^{--} ion is extremely small. We can thus assume $C_{\text{H}^+} = C_{\text{HS}^-}$. Now $C_{\text{H}_2\text{S}} = 0.1$,

$$\therefore C_{\text{H}^+} = C_{\text{HS}^-} = \sqrt{9 \times 10^{-8} \times 0.1} = 9.5 \times 10^{-5}$$

$$\text{Similarly, } C_{\text{S}^{--}} = \frac{K'_2 \times C_{\text{HS}^-}}{C_{\text{H}^+}} = K'_2 = 1 \times 10^{-15}$$

$$\text{Again, multiplying (a) with (b), we have } C_{\text{S}^{--}} = \frac{9 \times 10^{-24}}{C_{\text{H}^+}^2}$$

$\therefore$ In $0.25 M \text{HCl}$, assuming complete dissociation of HCl ,

$$C_{\text{S}^{--}} = \frac{9 \times 10^{-24}}{(0.25)^2} = 1.5 \times 10^{-22}$$

Thus we see, in aqueous solution, conc of H^+ ion was 9.5×10^{-5} and $C_{S--} = 1 \times 10^{-15}$. In $0.25 M$ HCl and C_{S--} is reduced to 1.5×10^{-23} .

Example 2. What is the effect of adding 0.25 gm-mole of NH_4Cl to a litre of $0.1 M$ ammonium hydroxide solution on the degree of dissociation of the base? $K_{NH_4OH} = 1.8 \times 10^{-5}$.

In $0.1 M$ NH_4OH solution, which is a very weak base, we have,

$$a = \sqrt{K_b/C} = \sqrt{1.8 \times 10^{-5}/0.1} = 0.0135$$

$$\therefore C_{OH^-} = C_{NH_4^+} = 0.00135, C_{NH_4OH} = 0.0986$$

Let a' be the degree of dissociation when 0.25 gm-mole of NH_4Cl was added. Then

$$C_{NH_4^+} = 0.25, C_{OH^-} = a'C = 0.1a', C_{NH_4OH} = (1-a')C \approx 0.1$$

since a' is quite small.

$$\therefore \frac{C_{NH_4^+} \cdot C_{OH^-}}{C_{NH_4OH}} = \frac{0.25 \times 0.1a'}{0.1} = 1.8 \times 10^{-5}$$

$$\text{or } a' = 7.2 \times 10^{-5}, \therefore C_{OH^-} = 7.2 \times 10^{-6}$$

i.e., degree of dissociation is reduced from 1.35% to 0.0072% .

Determination of Dissociation Constants. Two methods are usually employed for determining the dissociation constant of weak acids. The first method is based on conductance which has been discussed in Section XII.15, (eqn. XII.35).

The other method depends upon the determination of H^+ -ion concentration of solutions containing the weak acid and a salt of the same. Let us consider a solution of acetic acid (conc. C) also containing sodium acetate (conc. C_1). Let the concentration of hydrogen ion in the solution be C_{H^+} . Then,

$$\text{conc. of unionised acid, } HAc = C - C_{H^+}$$

$$\text{conc. of acetate ion} = C_1 + C_{H^+}$$

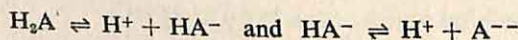
$$\text{Hence dissociation constant, } K_a' = \frac{C_{H^+} \cdot (C_1 + C_{H^+})}{(C - C_{H^+})}$$

A measurement of C_{H^+} will thus enable us to find out the dissociation constant as both C and C_1 are known. In a later section, the different methods for determining hydrogen ion concentrations will be discussed. The ionisation constants of weak bases are also determined in the same way.

The dissociation constants of acids and bases are often expressed in terms of logarithms called pK -values, where,

$$pK_a = -\log K_a, \quad pK_b = -\log K_b \quad \dots \text{ (XIII.47)}$$

Dissociation Constants of Weak Dibasic Acids. A few words may be mentioned also about the dissociation of dibasic acids. From organic dibasic acids, first only one hydrogen dissociates from a carboxyl group, and it follows the dilution law. The dissociation of the second carboxyl group takes place with considerable difficulty and only at very low concentrations. The two-stage dissociations are



So, the two dissociation constants are,

$$K_1 = \frac{C_{H^+} \cdot C_{HA^-}}{C_{H_2A}} \quad \dots (a) \quad K_2 = \frac{C_{H^+} \cdot C_{A^{--}}}{C_{HA^-}} \quad \dots (b)$$

The value of K_1 can be easily obtained from conductance measurement at ordinary concentrations. For determining K_2 , let us take a solution of the acid salt BAH at conc. C . The following equilibria are present :



In a dilute solution, when conc. of acid salt and neutral salt are negligible, we have,

$$C = C_{A^{--}} + C_{HA^-} + C_{H_2A} \quad \dots (c)$$

$$\text{and also from (ii) and (iv), } C_{A^{--}} = C_{H^+} + C_{H_2A} \quad \dots (d)$$

$$\text{from (c) and (d), } C_{HA^-} = C + C_{H^+} - 2C_{A^{--}} \quad \dots (e)$$

From equation (b)
$$C_{HA^-} = \frac{C_{H^+} \cdot C_{A^{--}}}{K_2} = C + C_{H^+} - 2C_{A^{--}}$$

or
$$C_{H^+} \cdot C_{A^{--}} = K_2 C + K_2 C_{H^+} - 2K_2 C_{A^{--}} \quad \dots (f)$$

From equations (a) and (d),
$$C_{HA^-} = \frac{K_1 C_{A^{--}} - K_1 C_{H^+}}{C_{H^+}} \quad \dots (g)$$

In (b) on substitution,
$$\frac{C_{H^+} \cdot C_{A^{--}}}{K_2} = \frac{K_1 C_{A^{--}} - K_1 C_{H^+}}{C_{H^+}}$$

or
$$C_{A^{--}} = \frac{K_1 K_2 C_{H^+}}{K_1 K_2 - C_{H^+}^2} \quad \dots (h)$$

Substituting in (f),
$$K_2 = \frac{[K_1 + C + C_{H^+}] C_{H^+}^2}{K_1 (C - C_{H^+})} \quad \dots (i)$$

When C_{H^+} is low,
$$K_2 = \frac{(K_1 + C) C_{H^+}^2}{K_1 C} \quad \dots (j)$$

By measuring K_1 conductometrically, and determining C_{H^+} of acid salt solution potentiometrically, K_2 is evaluated with the help of the relation (j).

TABLE : DISSOCIATION CONSTANTS OF ACIDS AND BASES AT 25°C

Acid/Base	Formula	K_a	pK_a
Formic	KCOOH	1.77×10^{-4}	3.75
Acetic	CH ₃ COOH	1.8×10^{-5}	4.75
Phenylacetic	C ₆ H ₅ CH ₂ COOH	4.8×10^{-5}	4.31
O-Chloro benzoic	C ₆ H ₄ Cl.COOH	1.2×10^{-3}	2.92
Benzoic	C ₆ H ₅ COOH	6.4×10^{-5}	4.2
Phenol	C ₆ H ₅ OH	1.2×10^{-10}	9.92
Hydrocyanic	HCN	7.2×10^{-10}	9.14
Iodic	HIO ₃	1.7×10^{-1}	0.77
Adipic	C ₄ H ₈ (COOH) ₂	$\begin{cases} K_1 = 3.7 \times 10^{-5} \\ K_2 = 3.8 \times 10^{-6} \end{cases}$	$\begin{matrix} 4.43 \\ 5.41 \end{matrix}$
Succinic	(CH ₂ COOH) ₂	$\begin{cases} K_1 = 6.6 \times 10^{-5} \\ K_2 = 2.5 \times 10^{-6} \end{cases}$	$\begin{matrix} 4.18 \\ 5.60 \end{matrix}$
Hydrogen sulphide	H ₂ S	$\begin{cases} K_1 = 9 \times 10^{-8} \\ K_2 = 1 \times 10^{-15} \end{cases}$	$\begin{matrix} 7.1 \\ 15.00 \end{matrix}$
Carbonic	H ₂ CO ₃	$\begin{cases} K_1 = 4.3 \times 10^{-7} \\ K_2 = 5.6 \times 10^{-11} \end{cases}$	$\begin{matrix} 6.4 \\ 10.3 \end{matrix}$
Oxalic	(COOH) ₂	$\begin{cases} K_1 = 5.9 \times 10^{-2} \\ K_2 = 6.4 \times 10^{-5} \end{cases}$	$\begin{matrix} 1.23 \\ 4.19 \end{matrix}$
Boric	H ₃ BO ₃	$K_1 = 5.8 \times 10^{-10}$	9.24
Phosphoric	H ₃ PO ₄	$\begin{cases} K_1 = 7.5 \times 10^{-3} \\ K_2 = 6.2 \times 10^{-8} \\ K_3 = 5 \times 10^{-13} \end{cases}$	$\begin{matrix} 2.12 \\ 7.2 \\ 12.3 \end{matrix}$
Citric	C ₃ H ₅ (COOH) ₃	$\begin{cases} K_1 = 9.2 \times 10^{-4} \\ K_2 = 2.69 \times 10^{-5} \\ K_3 = 1.4 \times 10^{-6} \end{cases}$	$\begin{matrix} 3.02 \\ 4.6 \\ 5.9 \end{matrix}$
Ammonium hydroxide	NH ₄ OH	1.8×10^{-5}	4.75
Silver hydroxide	AgOH	1.1×10^{-4}	3.96
Methyl amine	CH ₃ NH ₂	4.38×10^{-4}	3.36
Ethyl amine	C ₂ H ₅ NH ₂	4.6×10^{-4}	3.34
Pyridine	C ₅ H ₅ N	1.4×10^{-9}	8.85
Aniline	C ₆ H ₅ NH ₂	4.0×10^{-10}	9.40
Quinoline	C ₉ H ₇ N	6×10^{-10}	9.22

XIII.21. Ionic Product of Water. In the pure state, water is dissociated to a very small extent and behaves as a weak electrolyte. The equilibrium constant of the dissociation, $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$, is given by,

$$K = \frac{a_{\text{H}^+} \times a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} \quad \dots \text{(XIII.48)}$$

In the pure state or in dilute solution, the activity of water, $a_{\text{H}_2\text{O}}$ is constant and is taken as unity. Hence

$$a_{\text{H}^+} \times a_{\text{OH}^-} = K_w \quad \dots \text{(XIII.49)}$$

The constant K_w is called the *ionic activity product* of water.

Replacing activities with concentrations and activity coefficients,

$$K_w = C_{\text{H}^+} f_{\text{H}^+} \cdot C_{\text{OH}^-} f_{\text{OH}^-} = C_{\text{H}^+} \cdot C_{\text{OH}^-} f_{\text{H}^+} \cdot f_{\text{OH}^-}$$

or $K_w = K_w' \cdot f_{\text{H}^+} f_{\text{OH}^-}$

$$\dots \text{(XIII.50)}$$

where $K_w' = C_{\text{H}^+} C_{\text{OH}^-}$, called *ionic product* of water. $\dots \text{(XIII.51)}$

In pure water or in dilute solutions, the activity coefficients f_{H^+} and f_{OH^-} are almost unity, and so $K_w \approx K_w'$. That is, no appreciable error is involved in accepting ionic product of water as its ionic activity product. In concentrated solutions K_w' varies considerably but K_w remains constant, at any given temperature.

It has been seen in Sec. XII.15 (iii), that at 25°C, the concentration of H^+ ions in pure water is 1×10^{-7} . Since $C_{\text{H}^+} = C_{\text{OH}^-}$ in pure water, therefore

$$K_w' = C_{\text{H}^+} \cdot C_{\text{OH}^-} = (1 \times 10^{-7})^2 = 1 \times 10^{-14}$$

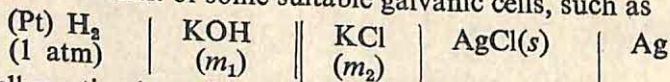
The equation (XIII.51) really suggests that in an aqueous medium, the product of the concentrations of H^+ and OH^- should be constant. If we are dealing, not with pure water, but a dilute aqueous solution, this relation is still valid. In an acid solution, there is a preponderance of H^+ ions but nevertheless there would be some OH^- ions, and the product of the two concentrations would be 1×10^{-14} at 25°C. Similarly in alkali solutions, there exist some H^+ ions. For example, in a M/100 HCl solution,

$$C_{\text{OH}^-} = \frac{C_{\text{OH}^-} \times C_{\text{H}^+}}{C_{\text{H}^+}} = \frac{K_w'}{C_{\text{H}^+}} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12}$$

Determination of Ionic Product of Water. (a) *From Conductance Measurement.*

The value of ionic product of water can be obtained by measuring the conductivity of pure water. This has been shown in Section XII.15.

(b) *E.m.f. Method.* The ionic product of water can be derived very accurately from measurement of e.m.f. of some suitable galvanic cells, such as



in which the cell reaction is, $\text{AgCl(s)} + \frac{1}{2}\text{H}_2 \rightarrow \text{Ag(s)} + \text{H}^+ + \text{Cl}^-$. So that its e.m.f.,

$$\begin{aligned} E &= E^\circ - \frac{RT}{f} \ln \frac{a_{\text{Ag(s)}} \cdot a_{\text{H}^+} \cdot a_{\text{Cl}^-}}{a_{\text{AgCl(s)}} \times a_{\text{H}_2}} \\ &= E^\circ - \frac{RT}{f} \ln a_{\text{H}^+} \cdot a_{\text{Cl}^-} \quad (\text{since } a_{\text{Ag}} = a_{\text{AgCl}} = a_{\text{H}_2} = 1) \end{aligned}$$

$$\begin{aligned} \therefore E &= E^\circ - \frac{RT}{f} \ln \frac{K_w \cdot a_{\text{Cl}^-}}{a_{\text{OH}^-}} \\ &= E^\circ - \frac{RT}{f} \ln K_w - \frac{RT}{f} \ln \frac{m_{\text{Cl}^-}}{m_{\text{OH}^-}} - \frac{RT}{f} \ln \frac{\gamma_{\text{Cl}^-}}{\gamma_{\text{OH}^-}} \end{aligned}$$

or $\left\{ E - E^\circ + \frac{RT}{f} \ln \frac{m_{\text{Cl}^-}}{m_{\text{OH}^-}} \right\} = - \frac{RT}{f} \ln K_w - \frac{RT}{f} \ln \frac{\gamma_{\text{Cl}^-}}{\gamma_{\text{OH}^-}}$

The value of E° is 0.2224 volts at 25°C.

The e.m.f. E of the cell is measured using various dilute solutions of KCl and KOH, i.e., with different low values of m_{Cl^-} and m_{OH^-} . The left-hand side of this equation is then plotted against the ratio of the ionic strength of the KCl and KOH

solutions used. The curve on extrapolation to infinite dilution of the solution, *i.e.*, zero ionic strength (where $\gamma_{\text{Cl}^-} = \gamma_{\text{OH}^-} = \text{unity}$), gives the value of $-\frac{RT}{f} \ln K_w$.

The value of K_w was thus found to be 1.008×10^{-14} at 25°C .

The ionic activity product (K_w) of water at different temperatures are,

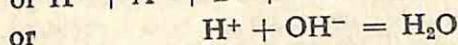
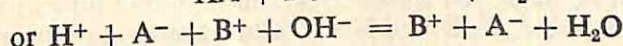
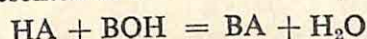
Temp. ($^\circ\text{C}$)	0°	18°	25°	40°	50°
$K_w \times 10^{14}$	0.114	0.578	1.008	2.919	5.344

The value of K_w is sometimes expressed in its logarithmic form, such that

$$pK_w = -\log K_w \quad \dots \text{(XIII.52)}$$

At 25°C , $pK_w = -\log (1 \times 10^{-14}) = 14$

Strong acids and strong alkalis as well as salts in dilute solution are taken as completely dissociated. Hence, the neutralisation of a strong acid with a strong alkali may be represented as :



In other words, neutralisation of strong acids with strong alkalis will be the union of H^+ ion with OH^- ion irrespective of the nature of the acid or alkali used, *i.e.*, independent of B^+ ions and A^- ions. Hence in any such neutralisation of strong acid—strong base, the heat of reaction should be the same. This has actually been experimentally observed. The constant heat of reaction of a strong base with a strong acid is -13690 calories at 20°C . (see Sec. IV.18 E).

If the ionic product of water at T_1 and T_2 temperatures are K_{w1} and K_{w2} , then using van't Hoff isochore, we have

$$\ln \frac{K_{w2}}{K_{w1}} = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 \cdot T_2} \right)$$

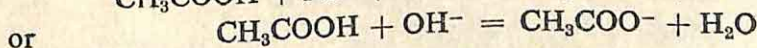
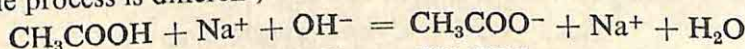
where ΔH is the heat of ionisation of water.

At 20°C , $K_{w1} = 0.681 \times 10^{-14}$, and at 30°C , $K_{w2} = 1.468 \times 10^{-14}$,

$$\text{hence } \log \frac{1.468}{0.681} = \frac{\Delta H}{2 \times 2.303} \cdot \frac{10}{(293 \times 303)}$$

$$\text{or } \Delta H = 13.6 \text{ kilocal.}$$

When a weak acid (say, CH_3COOH) is neutralised by an alkali, the heat of reaction is less, for the process is different,



Since the neutralisation here is not really H^+ and OH^- reaction and so the enthalpy-change is different and would depend on the nature of the acid used.

XIII.22. pH and pOH. In acid solutions the concentrations of H^+ ion are high and in alkaline solutions low. Sorensen suggested a new way of expressing this concentration of H^+ ions in logarithmic form so that negative exponents could be dispensed with. The negative of the logarithm of H^+ ion activity was defined as pH ;

$$\text{pH} = -\log a_{\text{H}^+} \quad \dots \text{(XIII.53)}$$

$$\text{i.e., } a_{\text{H}^+} = 10^{-\text{pH}} \quad \dots \text{(XIII.54)}$$

When the solution is very dilute, $a_{\text{H}^+} = C_{\text{H}^+}$, $\therefore \text{pH} = -\log C_{\text{H}^+}$.

Now for a solution of $\text{pH} = 3$, $C_{\text{H}^+} = 10^{-3}$ and for a solution of $\text{pH} = 8$, $C_{\text{H}^+} = 10^{-8}$.

In the same way, the activity (or concentration in dilute state) of OH^- ions is expressed in pOH scale, defined as

$$\text{pOH} = -\log a_{\text{OH}^-} \quad \dots (\text{XIII.55})$$

$$\text{or} \quad a_{\text{OH}^-} = 10^{\text{pOH}} \quad \dots (\text{XIII.56})$$

$$\text{Now} \quad a_{\text{H}^+} \cdot a_{\text{OH}^-} = K_w$$

$$\text{or} \quad -\log a_{\text{H}^+} - \log a_{\text{OH}^-} = -\log K_w = \text{p}K_w$$

$$\text{or} \quad \text{pH} + \text{pOH} = \text{p}K_w = \text{constant} \quad \dots (\text{XIII.57})$$

That is, as pH increases, pOH must decrease and *vice versa*.

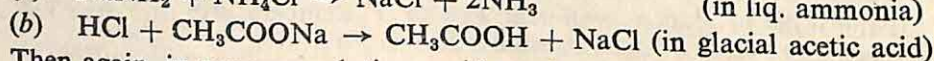
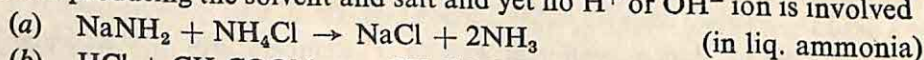
In pure water, which is neutral, $C_{\text{H}^+} = C_{\text{OH}^-} = 10^{-7}$ i.e., pH of water is 7.

Hence, the neutral solution has a pH = 7. Any solution having pH lower than seven will be acid and a solution having pH above seven will be alkaline. Thus at 25°C, pH of 0.00001 *m* KOH will be 9.0, for

$$C_{\text{H}^+} = \frac{K_w}{C_{\text{OH}^-}} = \frac{10^{-14}}{10^{-5}} = 10^{-9}, \text{ i.e., pH} = 9.$$

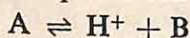
XIII.23. Generalised Concept of Acids and Bases. It would be useful now to mention briefly the modern ideas about acids and bases. Our general idea regarding acids and bases is based on Arrhenius concept in which an acid is defined as a compound which yields H^+ ions in aqueous solution and a base is a compound yielding OH^- ions in aqueous solution. Further, neutralisation of an acid with a base is really the union of H^+ and OH^- ions to form the solvent, water.

This definition though very useful in understanding acid-base reactions has its limitations. For example, reactions illustrated below are certainly neutralisation reactions producing the solvent and salt and yet no H^+ or OH^- ion is involved :

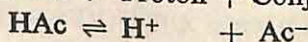
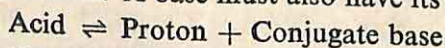


Then again, in aqueous solution, acids such as HClO_4 , HNO_3 , H_2SO_4 , HCl , etc. are all found completely dissociated and are regarded as almost equally strong. But when these acids are taken in glacial acetic acid medium, HClO_4 is found much stronger than nitric acid. Hence the solvent plays an important role in the manifestation of acid-base properties.

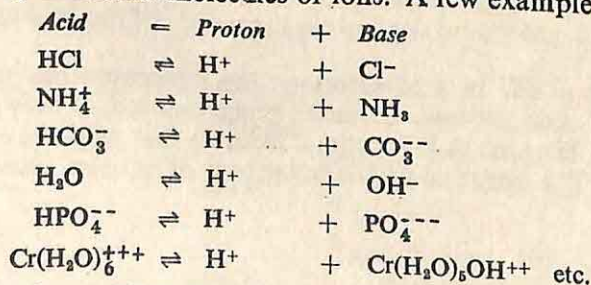
In 1923, Lowry and Brönsted advanced the protonic concept for acids and bases. According to this new concept, *an acid is defined as a substance which has a tendency to lose a proton (H^+) and a base is a substance which has a tendency to gain a proton*. The relationship between the two may be expressed as



where A is the acid and B its conjugate base. To function as acid, it must have the corresponding conjugate base. A base must also have its conjugate acid.



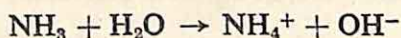
Acids and bases may be neutral molecules or ions. A few examples are cited :



The free proton is not likely to occur in solution. In water, the proton unites with a water molecule producing H_3O^+ , hydronium ion. In some other solvents also, proton associates with the solvent such as, $\text{CH}_3\text{COOH}_2^+$ (in glacial acetic acid), NH_4^+ ion (in liq. ammonia), $\text{CH}_3\text{CH}_2\text{OH}_2^+$ (in alcohol), etc.

In this text elsewhere, in treating the dissociation of acids, H^+ ion has been used as such for simplicity in writing equations, although properly H_3O^+ should have been used.

Water does function both as an acid and as a base. Water acts as an acid in presence of a base stronger than itself *e.g.*, ammonia ; it gives protons to ammonia.

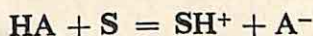


But in presence of acids stronger than itself water behaves as a base accepting a proton,



There are some other solvents which also play similar dualistic role in acid-base equilibria.

An acid will function as such only when it is in contact with some base *i.e.*, a proton acceptor. The base may be the solvent molecule as well. In other words, the acidic function will be manifest in presence of a solvent (S) with basic properties, such as,

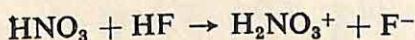


In fact both S and A^- tend to accept the proton. The degree of acidity depends upon the relative capabilities of S and A^- in accepting the proton. An acid is strong when the tendency of the anion A^- to accept a proton is less than that of the solvent S, as in HCl. And the acid will be weak when the anion A^- is quite keen to accept the proton as in acetic acid. In the same way a strong base is one having greater tendency to accept protons than the solvent molecules.

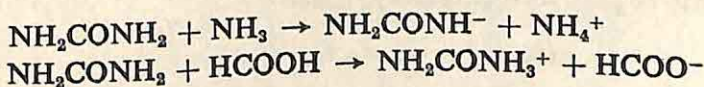
It is obvious that solvent would affect the acid-base character of a substance profoundly. From this point the solvents may be of four types :

Solvent	Character	Examples
(a) protophylic	tendency to accept protons	NH_3 , NH_2OH , RNH_2 , etc.
(b) protogenic	tendency to release protons	H_2SO_4 , HAc , $HCOOH$, HF , etc.
(c) amphiprotic	capable of both losing and gaining protons	H_2O , C_2H_5OH , etc.
(d) aprotic	no tendency either to lose or gain protons	C_6H_6 , CCl_4 , $CHCl_3$, etc.

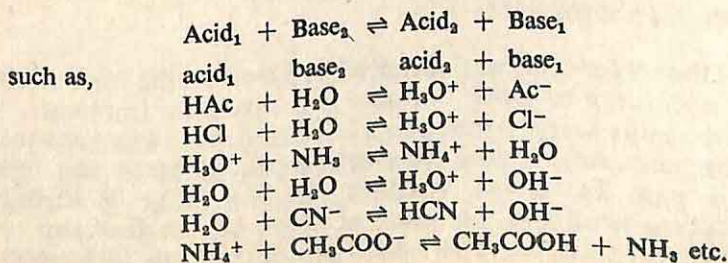
Thus, HNO_3 acts as an acid in aqueous media losing a proton. But it behaves as a base by accepting a proton in anhydrous HF.



Again urea behaves as an acid in liq. ammonia but as a base in anhydrous formic acid,

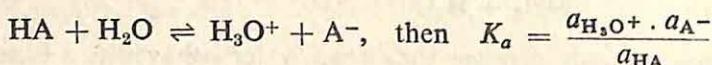


It is also evident that the interaction between an acid (HA) and a base (H_2O) leads to the formation of another acid (H_3O^+) conjugate to the base and a base (A^-) conjugate to the acid. This is generally true.



The beauty of the Lowry Brönsted theory lies in the fact that it contains all effects of Arrhenius concept and further extends to include and explain other types of acid-base equilibria even in non-aqueous media. A consideration of the dissociation constant will be more revealing.

Suppose we have an acid (HA) in aqueous medium,

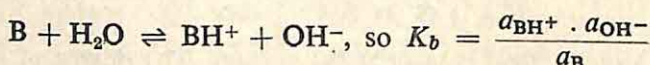


Since the whole of proton is present as H_3O^+ , we may write

$$K_a = \frac{a_{\text{H}^+} \cdot a_{\text{A}^-}}{a_{\text{HA}}}$$

This is the same as the conventional dissociation constant. That is, Lowry-Brönsted concept gives the same result.

Again, suppose a base B is taken in aqueous medium,



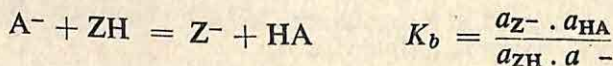
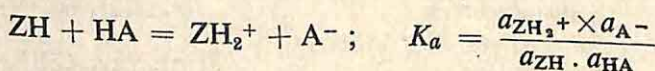
In the classical fashion, we write, $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BOH} \rightleftharpoons \text{BH}^+ + \text{OH}^-$

$$\text{or } K_b' = \frac{a_{\text{BH}^+} \cdot a_{\text{OH}^-}}{a_{\text{BOH}}} = \frac{a_{\text{BH}^+} \cdot a_{\text{OH}^-}}{a_{\text{B}}}$$

for whole of unreacted B is present as BOH.

Hence, the conventional dissociation constant and the Lowry-Brönsted K_b are the same.

Moreover, suppose ZH is a solvent amphiprotic in character. Its reaction with an acid and its conjugate base would be as follows.



Hence

$$K_a K_b = \frac{a_{\text{ZH}_2^+} \cdot a_{\text{Z}^-}}{a_{\text{ZH}}^2}$$

But a_{ZH} , activity of pure solvent is unity, hence

$$a_{\text{ZH}_2^+} \cdot a_{\text{Z}^-} = K_a K_b = K_j,$$

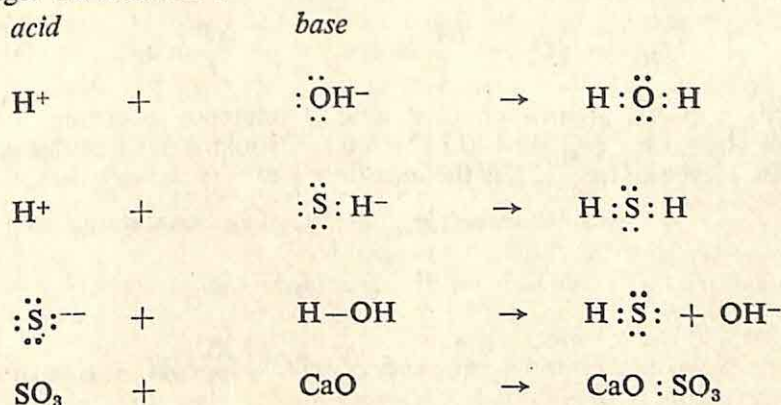
called ionic product of the solvent. In water,

$$K_a K_b = a_{\text{H}_3\text{O}^+} \cdot a_{\text{OH}^-} = a_{\text{H}^+} \cdot a_{\text{OH}^-} = K_w.$$

We have already seen K_w is a constant.

A more general theory for acids was advanced by Lewis on the basis of electron theory of valence. According to Lewis, an acid is a substance (molecule, ion or radical) which would readily accept a lone pair of electrons from a donor substance, which would be the base. Acid is thus an electron-pair acceptor and base is a donor of electron pair. Thus, the reaction, $\text{Et}_3\text{N} + \text{BCl}_3 \rightarrow \text{Et}_3\text{N} : \text{BCl}_3$ is definitely an acid-base neutralisation reaction which can be followed with an indicator in chlorobenzene solution. There is no proton, nor any OH group.

It is thus seen that neutralisation virtually means the formation of a co-ordinate linkage. To illustrate :



This theory covers all acids of the protonic concept and other substances too. The acidic properties of non-metallic oxides and the basic properties of metal oxides are also explained.

XIII.24. Determination of pH or H^+ ion Concentration. The concentration of H^+ ions of a solution can be determined from conductance measurement when the solution contains only a weak acid or weak alkali as solute. This has been illustrated in the previous chapter. We shall see in a subsequent section the colorimetric method for the determination of pH in which the colour of the solution with a suitable indicator is compared to that produced by a buffer solution of known pH. The most accurate method of ascertaining the pH of a solution depends on e.m.f. measurement. The given solution is made the electrolyte of a half-cell such that its potential is governed by the H^+ ion concentration of the solution. This half-cell is then coupled with a reference electrode and the e.m.f. of the cell is measured potentiometrically. Three different types of half-cells or single electrodes are commonly used and we may consider these separately.

(a) *Hydrogen Electrode.* An arrangement, as shown in Fig. XIII.12, is made in which the solution whose pH is to be determined is taken in a pyrex vessel

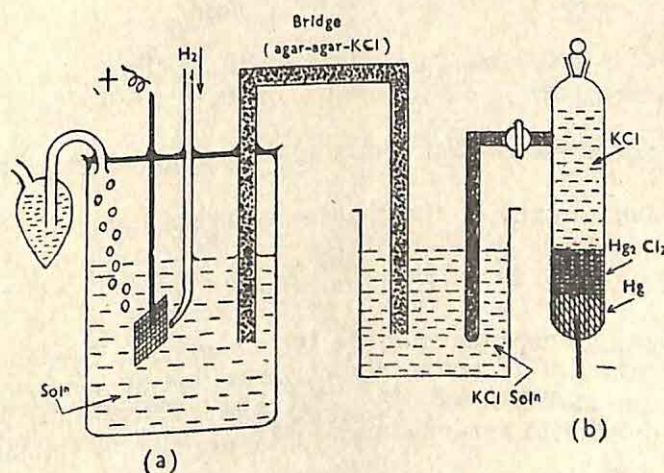


FIG. XIII.12 Determination of pH

provided with a lid. Through the lid is introduced a Pt wire carrying Pt-foil coated with Pt-black and kept immersed in the solution. Pure H_2 -gas at 1 atmosphere is continuously bubbled so that the Pt-black and the solution are saturated and at eqm. Precautions are essential to ensure that external atmospheric gases do not diffuse into the system. The temperature is maintained constant by placing

it in a thermostat. It is thus a hydrogen electrode; and if a_{H^+} is the activity of hydrogen ions in the given solution then its electrode potential would be,

$$\xi_{H_2} = \xi_{H_2}^0 - \frac{RT}{f} \ln a_{H^+} = - \frac{RT}{f} \ln a_{H^+} \quad (\text{since } \xi_{H_2}^0 = 0)$$

This half-cell is now coupled with a reference electrode, say a saturated calomel electrode ($\xi_{Cal} = -0.242$ volts), through a KCl bridge so that junction potential is eliminated. If E is the measured e.m.f. of the cell, then,

$$E = \xi_{H_2} - \xi_{Cal} \quad (\xi's \text{ containing their own signs})$$

$$= - \frac{RT}{f} \ln a_{H^+} - \xi_{Cal}$$

$$= - \xi_{Cal} + 2.303 \frac{RT}{f} \text{pH} \quad (\text{for } -\log a_{H^+} = \text{pH})$$

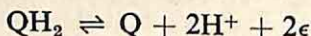
$$\text{i.e.,} \quad \text{pH} = \frac{f(E + \xi_{Cal})}{2.303 RT} = \frac{E + \xi_{Cal}}{0.059} \quad (\text{at } 25^\circ\text{C})$$

The pH of the solution can thus be evaluated. The hydrogen electrode is not suitable when the solution contains an oxidising agent or ions of nobler metals (e.g., Cu, Ag, etc), or unsaturated organic compounds.

(b) *Quinhydrone Electrode*. Quinhydrone is an equimolecular compound of quinone and hydroquinone and when placed in a solution, the equilibrium may be represented as



This is indeed an oxidation-reduction system and if a Pt-wire is dipped in it, a redox single-electrode is formed. Writing 'Q' for $C_6H_4O_2$, we have



The equilibrium evidently depends upon the H^+ ion concentration. The e.m.f. of the single electrode potential is given by

$$\begin{aligned} \xi_Q &= \xi_Q^0 - \frac{RT}{2f} \ln \frac{a_Q \cdot a_{H^+}^2}{a_{QH_2}} \\ &= \xi_Q^0 - \frac{RT}{2f} \ln \frac{a_Q}{a_{QH_2}} - \frac{RT}{f} \ln a_{H^+} \end{aligned}$$

In practice by keeping the solution saturated with quinhydrone, the ratio $\frac{a_Q}{a_{QH_2}}$ is maintained constant at unity, so that the electrode potential is

$$\xi_Q = \xi_Q^0 - \frac{RT}{f} \ln a_{H^+}$$

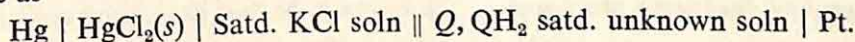
The potential therefore depends upon the H^+ ion activity. The value ξ^0 is determined with a solution of known H^+ ion concentration by measuring e.m.f. after coupling with a standard half-cell. ξ_Q^0 is taken as 0.699 volts at 25°C . This electrode is then coupled with a calomel electrode (ξ_{Cal}) and the e.m.f. of the cell (E) is measured.

$$E = \xi_{Cal} - \left[\xi_Q^0 - \frac{RT}{f} \ln a_{H^+} \right] = \xi_{Cal} - \xi_Q^0 + 2.303 \frac{RT}{f} \log a_{H^+}$$

$$\text{or} \quad -2.303 \frac{RT}{f} \log a_{H^+} = \xi_{Cal} - \xi_Q^0 - E$$

$$\text{or} \quad \text{pH} = \frac{\xi_{Cal} - \xi_Q^0 - E}{2.303 RT/f} \quad \dots \text{(XIII.58)}$$

To the solution in a beaker is added a small quantity of quinhydrone (1 gm per 100 c.c.) and stirred well to ensure saturation. A Pt-wire or a bright Pt-foil is suspended in the solution. This is one half-cell which is connected through a salt bridge (an inverted U-tube filled with KCl-agar jelly) to the reference calomel electrode as



The e.m.f. (E) is measured and then pH is evaluated from equation (XIII.58).

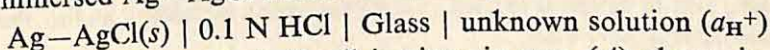
The quinhydrone electrode has many advantages over hydrogen electrode. Its simplicity and quick attainment of reversible equilibrium are of utmost importance. A small quantity of solution is sufficient and air need not be excluded. It can also be used in presence of heavier ions or unsaturated organic substances where hydrogen electrode cannot be applied. But quinhydrone electrodes cannot be used in alkaline solutions above pH, 8.5.

(c) *Glass Electrode.* The most commonly used electrode for pH determination now-a-days is the glass electrode. Haber and Klemensiewicz showed that if a thin glass membrane separates two solutions a potential is developed across the membrane. The magnitude of this membrane potential depends chiefly on the pH of the solutions. If one of the solutions be kept constant and the pH of the other solution varied, then the electrode potential follows the relation.

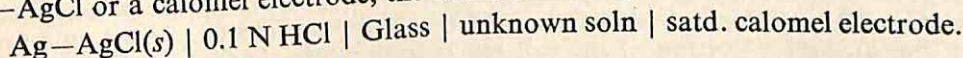
$$\xi_G = \xi_G^\circ - \frac{RT}{f} \ln a_{H^+} \quad \dots (A)$$

That means the electrode functions in the same way as a hydrogen electrode.

The glass electrode consists of a thin membrane of a specially prepared soft glass globe containing a dilute solution of hydrochloric acid (or $\text{KCl} + \text{CH}_3\text{COOH}$), in which is immersed Ag-AgCl electrode. That is, the electrode is



The electrode potential of this half cell is given in eqn. (A) above, in which ξ_G° includes a small 'asymmetry potential' which exists across the glass membrane due to internal strain. When this electrode is coupled with a reference electrode, say a Ag-AgCl or a calomel electrode, the cell obtained is,



The e.m.f. of this cell is

$$E = \xi_G - \xi_{\text{Cal}} = \xi_G^\circ + 2.303 \frac{RT}{f} \text{pH} - \xi_{\text{Cal}}$$

In practice, the assembly of glass electrode is first used with a solution of known pH, say $\text{pH}_{(1)}$, and its e.m.f. is E_1 . This solution is then substituted with the unknown

solution. So that, $\Delta E = E_1 - E = 2.303 \frac{RT}{f} (\text{pH}_{(1)} - \text{pH})$

It is thus immaterial what reference electrode is employed provided the same is used in both the measurements.

The glass electrode and the reference electrode are suspended in the given solution as shown in Fig. XIII.13 and the e.m.f. of the cell measured with an electronic voltmeter. Ordinary potentiometer cannot be used due to the very high resistance of the glass-membrane. The advantage of the glass electrode is that it can be used in any solution not being affected by organic compounds or oxidising or reducing agents. A small quantity of the solution is sufficient for the determination of pH. Special glass membranes are required when the pH of the solution is very high ($\text{pH} > 10$).

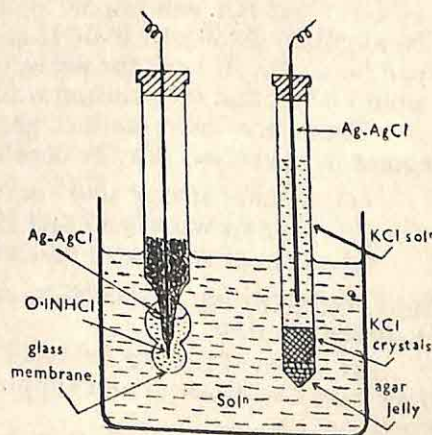


FIG. XIII.13 Use of glass electrode

XIII.25. Isohydric Solutions. The dissociation of a weak electrolyte is generally suppressed to some extent by the addition of a common ion. But it is possible to mix two solutions of different weak acids without the dissociation of either being affected. Such acid solutions whose dissociations are not changed on mixing are said to be *isohydric* with one another.

Suppose two such weak acid solutions HA_1 and HA_2 have concentrations c_1 and c_2 , in which their degrees of dissociation are α_1 and α_2 . Let k_1 and k_2 be their dissociation constants. Then

$$k_1 = \frac{\alpha_1^2 c_1}{1 - \alpha_1} \quad \text{and} \quad k_2 = \frac{\alpha_2^2 c_2}{1 - \alpha_2}$$

Let v_1 litres of HA_1 solution be mixed with v_2 litres of HA_2 solution. On mixing, as degrees of dissociation remain constant and the total volume is $(v_1 + v_2)$, hence,

$$C_{H^+} = \frac{\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2}{v_1 + v_2} \quad \text{and} \quad C_{A_1^-} = \frac{\alpha_1 c_1 v_1}{v_1 + v_2}, \quad C_{HA_1} = \frac{(1 - \alpha_1) c_1 v_1}{v_1 + v_2}$$

$$\therefore k_1 = \frac{C_{H^+} \cdot C_{A_1^-}}{C_{HA_1}} = \frac{(\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2) \alpha_1}{(v_1 + v_2)(1 - \alpha_1)}$$

Comparing with the earlier expression of k_1 , we have

$$\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2 = \alpha_1 c_1 (v_1 + v_2)$$

Similarly, considering the other acid HA_2 , the expression would be

$$\alpha_1 c_1 v_1 + \alpha_2 c_2 v_2 = \alpha_2 c_2 (v_1 + v_2)$$

hence

$$\alpha_1 c_1 = \alpha_2 c_2$$

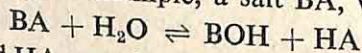
i.e.,

$$C_{H^+ (1)} = C_{H^+ (2)}$$

... (XIII.59)

Hence it is seen that two weak acid solutions would be isohydric when their hydrogen ion concentrations are the same before mixing. It depends in no way on the volumes of the solutions mixed. Such conditions may be extended to weak electrolytes having common ion other than acids which may be termed iso-ionic solutions.

XIII.26. Hydrolysis of Salt Solutions. The solutions of *neutral* salts in water are not often found neutral in reaction. In many cases such aqueous solutions of salts are either alkaline or acidic to litmus. Thus a solution of ammonium chloride is acidic and a solution of potassium cyanide alkaline to litmus. This is due to the fact that at least a portion of the salt reacts with water to produce back the acid and the base from which the salt was obtained, i.e., a process opposite to that of neutralisation occurs. This process of decomposition of the salt by water is *hydrolysis*. If the acid and the base produced by hydrolysis are not both strong, in other words if one of them be weak, their strengths would be different. The ionisation of the acid and base being unequal, the resulting solution due to hydrolysis would be acidic or alkaline. Consider, for example, a salt BA, which reacts with water as



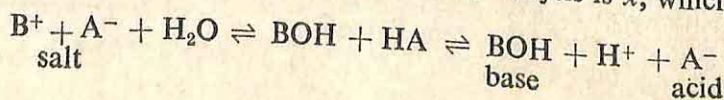
If BOH is a strong base and HA a weak acid, then BOH will produce large quantities of OH^- but HA will remain practically undissociated. The resulting solution will be alkaline. Similarly, if BOH is weak and HA is strong, it is obvious the solution will be acidic. If both the parent acid and base of the salt are strong, no hydrolysis would occur and the solution would be neutral as in the case of HCl.

There are three distinct groups of salts suffering hydrolysis, for which the extent of hydrolysis may be considered separately ;

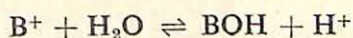
- salts of strong acid and weak base
- salts of weak acid and strong base
- salts of weak acid and weak base.

Salts, being strong electrolytes, are supposed to be practically completely ionised in dilute solutions.

(a) **Salts of Strong Acid and Weak Base.** Let BA be such a salt which hydrolyses partly with water and suppose the degree of hydrolysis is x , which is usually small.



The acid, being strong and present in small concentration, is supposed to be fully ionised. Hence we may write,



Suppose c is the initial concentration of the salt.

The equilibrium constant, called the hydrolytic constant K_h is given by,

$$\begin{aligned} K_h &= \frac{a_{BOH} \cdot a_{H^+}}{a_{B^+} \cdot a_{H_2O}} = \frac{a_{BOH} \cdot a_{H^+}}{a_{B^+}} \quad (a_{H_2O} = 1) \\ &= \frac{C_{BOH} \cdot C_{H^+}}{C_{B^+}} \cdot \frac{f_{BOH} \cdot f_{H^+}}{f_{B^+}} \end{aligned}$$

In solutions of low ionic strength, $\frac{f_{H^+}}{f_{B^+}} \approx 1$, and $f_{BOH} = 1$.

$$\therefore K_h = \frac{C_{BOH} \cdot C_{H^+}}{C_{B^+}} \quad \dots \text{(XIII.60)}$$

Now $C_{BOH} = cx$, $C_{H^+} = cx$ and $C_{B^+} = c(1-x)$

$$\therefore K_h = \frac{cx \cdot cx}{c(1-x)} = \frac{cx^2}{1-x} \quad \dots \text{(XIII.61)}$$

That is, degree of hydrolysis x can be evaluated if K_h is known. When x is quite small, we have

$$K_h \approx cx^2 \text{ or } x = \sqrt{K_h/c} \quad \dots \text{(XIII.62)}$$

The equation (XIII.60) may be written also as

$$K_h = \frac{C_{BOH} \cdot C_{OH^-} \cdot C_{H^+}}{C_{B^+} \cdot C_{OH^-}} = \frac{K_w}{K_b} \quad \dots \text{(XIII.63)}$$

The concentration of the H^+ ions is cx ,

$$\therefore C_{H^+} = cx = \sqrt{K_h \cdot c} \quad (\text{from equation XIII.62})$$

$$\text{or } C_{H^+} = \sqrt{\frac{K_w}{K_b} \cdot c} \quad (\text{from equation XIII.63})$$

Taking logarithms of the inverse of both sides,

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c \quad \dots \text{(XIII.64)}$$

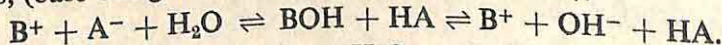
Illustration : The pH of a 0.02 M NH_4Cl solution will be given by,

$$pH = \frac{1}{2} \times 14.0 - \frac{1}{2} (4.74) - \frac{1}{2} (\log 2 \times 10^{-2}) = 5.48$$

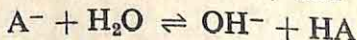
(for, $K_{NH_4OH} = 1.85 \times 10^{-5}$ or $pK_{NH_4OH} = 4.74$)

$$\therefore x = \frac{C_{H^+}}{c} = \sqrt{\frac{K_w}{K_b c}} = \sqrt{\frac{10^{-14}}{1.85 \times 10^{-5} \times 0.02}} = 5 \times 10^{-3}$$

(b) **Salts of Weak Acid and Strong Base.** The hydrolytic equation may be represented as, (base being assumed fully ionised as the salt),



or



Hence the hydrolytic constant (K_h) is given by

$$\begin{aligned} K_h &= \frac{a_{OH^-} \cdot a_{HA}}{a_{A^-} \cdot a_{H_2O}} = \frac{a_{OH^-} \cdot a_{HA}}{a_{A^-}} \\ &= \frac{C_{OH^-} \cdot C_{HA}}{C_{A^-}} \cdot \frac{f_{OH^-} \cdot f_{HA}}{f_{A^-}} \end{aligned}$$

At low ionic strength, $f_{\text{HA}} = 1$, and also $\frac{f_{\text{OH}^-}}{f_{\text{A}^-}} \approx 1$,

$$\therefore K_h = \frac{C_{\text{OH}^-} \cdot C_{\text{HA}}}{C_{\text{A}^-}} \quad \dots \text{(XIII.65)}$$

If c be the original concentration of salt and if x be the degree of hydrolysis, then

$$C_{\text{OH}^-} = cx, \quad C_{\text{HA}} = cx, \quad C_{\text{A}^-} = c(1-x).$$

That is,

$$K_h = \frac{cx \cdot cx}{c(1-x)} = \frac{x^2 c}{1-x} \quad \dots \text{(XIII.66)}$$

When x is small, $K_h = x^2 c$, hence $x = \sqrt{K_h/c}$... (XIII.67)

From eqn (XIII.65), we find

$$K_h = \frac{C_{\text{OH}^-} \cdot C_{\text{HA}}}{C_{\text{A}^-}} = \frac{C_{\text{OH}^-} \cdot C_{\text{HA}} \cdot C_{\text{H}^+}}{C_{\text{A}^-} \cdot C_{\text{H}^+}} = \frac{K_w}{K_a} \quad \dots \text{(XIII.68)}$$

$$\therefore \text{degree of hydrolysis, } x = \sqrt{\frac{K_w}{K_a c}} \quad \dots \text{(XIII.69)}$$

$$\text{and conc. of OH}^- \text{ ions, } C_{\text{OH}^-} = cx = \sqrt{\frac{K_w \cdot c}{K_a}}$$

$$\therefore C_{\text{H}^+} = \frac{K_w}{C_{\text{OH}^-}} = \sqrt{\frac{K_w \cdot K_a}{c}}$$

Taking the negatives of logarithms on both sides,

$$\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c \quad \dots \text{(XIII.70)}$$

To illustrate : The pH of a sodium acetate solution (0.01 M) is given by,

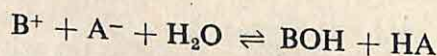
$$\begin{aligned} \text{pH} &= \frac{1}{2} \times 14 + \frac{1}{2}(4.74) + \frac{1}{2} \log 10^{-2} \\ &= 7 + 2.37 - 1 = 8.37. \end{aligned}$$

(for, $K_{\text{acetic acid}} = 1.8 \times 10^{-5}$, i.e., $\text{p}K_a = 4.74$)

$$\text{The hydrolytic constant, } K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

$$\text{and degree of hydrolysis, } x = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{5.5 \times 10^{-10}}{1 \times 10^{-2}}} = 2.35 \times 10^{-4}$$

(c) **Salts of Weak Acid and Weak Base.** In this case the products of hydrolysis are both weak and hence would be almost undissociated. The hydrolytic equilibrium is expressed as,



So that, the hydrolytic constant is

$$K_h = \frac{a_{\text{BOH}} \times a_{\text{HA}}}{a_{\text{B}^+} \cdot a_{\text{A}^-} \cdot a_{\text{H}_2\text{O}}} \quad (a_{\text{H}_2\text{O}} = 1)$$

If the activity coefficient of undissociated molecules as also, less justifiably, those of ions be taken as unity in dilute solutions,

$$K_h = \frac{C_{\text{BOH}} \times C_{\text{HA}}}{C_{\text{B}^+} \times C_{\text{A}^-}} \quad \dots \text{(XIII.71)}$$

$$\text{or} \quad K_h = \frac{C_{\text{BOH}}}{C_{\text{B}^+} \cdot C_{\text{OH}^-}} \cdot \frac{C_{\text{HA}}}{C_{\text{A}^-} \cdot C_{\text{H}^+}} \cdot C_{\text{H}^+} \cdot C_{\text{OH}^-}$$

$$\text{i.e.,} \quad K_h = \frac{K_w}{K_a K_b} \quad \dots \text{(XIII.72)}$$

Also from (XIII.71), if c be the conc. of the salt solution and x the degree of hydrolysis,

$$K_h = \frac{cx \times cx}{c(1-x) \cdot c(1-x)} = \left(\frac{x}{1-x} \right)^2 \quad \dots \text{(XIII.73)}$$

So, the degree of hydrolysis and the pH of the solution are independent of the concentration.

Further, we know for the weak acid,

$$K_a = \frac{C_{\text{H}^+} \cdot C_{\text{A}^-}}{C_{\text{HA}}} \quad \text{or} \quad C_{\text{H}^+} = K_a \cdot \frac{C_{\text{HA}}}{C_{\text{A}^-}}$$

$$\therefore C_{\text{H}^+} = K_a \frac{cx}{c(1-x)} = K_a \cdot \frac{x}{1-x}$$

$$\text{Applying eqn (XIII.73)} \quad C_{\text{H}^+} = K_a \sqrt{K_h} = K_a \sqrt{\frac{K_w}{K_a K_b}}$$

$$\text{or} \quad C_{\text{H}^+} = \sqrt{\frac{K_w \cdot K_a}{K_b}}$$

$$\text{Hence} \quad \text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b \quad \dots \text{(XIII.74)}$$

When the dissociation constants are equal, i.e.,

$\text{p}K_a = \text{p}K_b$; $\text{pH} = 7.0$, the resulting solution is neutral;

when $K_a > K_b$; $\text{pH} < 7.0$, the solution is acidic;

and when $K_a < K_b$, $\text{pH} > 7.0$ the solution is alkaline.

Given

$$K_{\text{CH}_3\text{COOH}} = 1.8 \times 10^{-5}, K_{\text{NH}_4\text{OH}} = 1.8 \times 10^{-5}, K_{\text{HCN}} = 7.2 \times 10^{-10}$$

The pH of ammonium acetate solution: $\text{pH} = 7.0 + 2.37 - 2.37 = 7.0$ i.e., the solution would be practically neutral.

The pH of ammonium cyanide solution: $\text{pH} = 7.0 + 4.57 - 2.37 = 9.20$ i.e., the solution would be alkaline.

XIII.27. Determination of Hydrolysis Constant.

(a) *Conductivity Method.* The conductance of a solution of a salt from a weak acid or a weak base is due partly to the ions of the salt and partly to the ions of the acid or the base formed by hydrolysis. Suppose we consider a salt like aniline hydrochloride formed from a weak base. If c be the concentration of the salt solution and x its degree of hydrolysis, then

$$c \cdot \lambda = c(1-x)\lambda_s + cx\lambda_{\text{HA}}$$

i.e., total conductance is the sum of conductances of $c(1-x)$ gm-eqv. of unhydrolysed salt and cx gm equivalents of free acid. λ is the apparent equivalent conductance of the salt in solution which is directly measured. The relation above may be transformed as

$$x = \frac{\lambda - \lambda_s}{\lambda_{\text{HA}} - \lambda_s} \quad \dots \text{(XIII.75)}$$

The value λ_{HA} may be taken as $\lambda_{\text{H}^+} + \lambda_{\text{A}^-}$ i.e., $\lambda_{0\text{HA}}$ at infinite dilution; or still better the eqv. conductance of HA may be separately measured at a total ionic strength as existing in the experimental salt solution.

For the determination of λ_s , the conductance of the unhydrolysed salt, excess of free base aniline is added to the salt solution until the hydrolysis is repressed to a negligible amount. Under this condition, assuming the free base does not materially contribute to the conductivity, λ_s is experimentally found out. Now that λ , λ_s and λ_{HA} are all known, the degree of hydrolysis x is evaluated by equation (XIII.75). The value of hydrolysis constant (K_h) can be computed with equation (XIII.62).

For example : The equivalent conductance of 0.011 solution of aniline hydrochloride is 120 mhos. When the solution is saturated with excess aniline, the equivalent conductance drops to 104 mhos. The equivalent conductance of HCl at the same concentration is 410 mhos. What are the degree of hydrolysis and the hydrolytic constant ?

$$x = \frac{\lambda - \lambda_s}{\lambda_{HA} - \lambda_s} = \frac{120 - 104}{410 - 104} = 0.052$$

$$\therefore K_h = cx^2 = 0.011 \times (0.052)^2 = 3.0 \times 10^{-5}$$

(b) *pH-determination Method.* When a salt solution undergoes hydrolysis, the degree of hydrolysis is related to the pH of the solution. We have seen, if it is a salt derived from a weak base-strong acid, then, $C_{H^+} = cx$, where x is the degree of hydrolysis. Otherwise, if it be a salt derived from a strong base-weak acid, $C_{OH^-} = cx$, i.e., $C_{H^+} = K_w/cx$.

In practice the salt solution is taken and its pH is determined with the help of a glass electrode as in section XIII.24. The conc. of H^+ -ion in the solution is known. From this, the degree of hydrolysis x or the hydrolytic constant K_h can be easily computed.

When the salt is formed from a weak acid-weak base, $C_{H^+} = K_a \sqrt{K_h}$. So the dissociation constant of the acid must also be separately determined.

(c) *Distribution Method.* When one of the products of hydrolysis of a salt in solution is soluble in another solvent immiscible with water while the salt and other components are not soluble in the other solvent, partition coefficient measurements are utilised for determination of hydrolytic constant. To illustrate : The salt aniline hydrochloride undergoes hydrolysis and if its aqueous solution is shaken with benzene, aniline distributes itself between benzene and water, but the salt or hydrochloric acid is practically insoluble in benzene.

In practice, aniline hydrochloride solution of known concentration (c_1) is taken and shaken with benzene. The volume of benzene added is v litres per litre of the aqueous solution. Let (c_2) be the concentration of base aniline (estimated) in the benzene layer. Suppose, the partition coefficient of aniline between benzene

and water, $P = \frac{C_{\text{water}}}{C_{\text{benzene}}} = \frac{c_w}{c_2}$

i.e., in aqueous layer, conc. of aniline $c_w = P.c_2$.

The free base in benzene = c_2v

The free base in water = $P.c_2$

$\therefore$ Total free base = $c_2v + Pc_2$

In water, the conc. of unhydrolysed salt = $c_1 - c_2v - Pc_2$

The conc. of free acid in water = total amount of free base = $c_2v + Pc_2$

Hence, the hydrolytic constant,

$$K_h = \frac{C_{\text{acid}} \times C_{\text{base in water layer}}}{C_{\text{unhydrolysed salt}}} = \frac{(c_2v + Pc_2).Pc_2}{(c_1 - c_2v - Pc_2)}$$

All the quantities on the rt-hand side are known, hence K_h is easily evaluated. The value of P is separately determined.

(d) *Indirect Method.* When dissociation constants of the weak acid and weak base are known, the hydrolytic constant of a salt from the corresponding acids

and bases can be computed with the help of equations (XIII.63, 68, 72). The degree of hydrolysis can then be evaluated from K_h -values.

XIII.28. Buffers. If we add 1 c.c. of a 0.01 N HCl to a litre of water, the pH of the solution changes from 7 to 5. But if we add the same to a litre of ammonium acetate solution, the pH practically remains unaltered at 7.0. The resistance of a solution to changes in H^+ ion concentration upon the addition of small amounts of acid or alkali is termed 'buffer action'. Solutions which possess such properties are known as "buffer solutions", or simply, *buffers*. The buffer solutions have thus 'reserve acidity and reserve alkalinity'.

Buffer solutions usually consist of mixtures of solutions of a weak acid or base and its salt. The buffer action can be understood in the following way. Suppose we have a mixture of acid HA and its salt BA in solution. The ionisation equilibrium determines the H^+ ion concentration.

$$K_a = \frac{C_{H^+} \cdot C_{A^-}}{C_{HA}} \quad \text{or} \quad C_{H^+} = \frac{C_{HA}}{C_{A^-}} \cdot K_a \quad \dots (A)$$

To the solution now if we add H^+ ions in the form of an acid, these H^+ ions would be removed as HA by combining with A^- of the salt. This is necessary to maintain the above ionisation equilibrium, and so pH remains practically undisturbed. On the other hand if some alkali is added to the buffer solution, the added OH^- ions disturb the ionisation equilibrium of water. So OH^- ions and H^+ ions combine to form H_2O . In order to maintain acid ionisation equilibrium, some HA will dissociate to compensate for the H^+ ions removed. Here again the pH of the solution would remain at the initial level. In the same way, the buffering action of a mixture of weak base BOH and its salt BA can be explained. Such considerations are however applicable only when the added acid or alkali are not too large in comparison with the amounts of the salt or acid of the buffer.

Suppose a buffer is composed of an acid HA of concentration C_a and its salt BA of concentration C_s . Let C_{H^+} be the concentration of the H^+ ions in the buffer. Then, conc. of undissociated acid = $C_a - C_{H^+}$ and since the solution is electrically neutral, and the salt is assumed completely dissociated,

$$\text{conc. of anion, } C_{A^-} = C_s + C_{H^+}.$$

Substituting these in (A) above,

$$C_{H^+} = K_a \frac{C_a - C_{H^+}}{C_s + C_{H^+}} \quad \dots (B)$$

This quadratic equation when solved gives the value of the C_{H^+} of the buffer. But the acid is weak and further its dissociation is repressed by the salt, hence C_{H^+} is quite small compared to C_a or C_s . Hence

$$C_{H^+} = K_a \cdot \frac{C_a}{C_s} = K_a \cdot \frac{C_{acid}}{C_{salt}}$$

$$\text{or} \quad pH = pK_a + \log \frac{C_{salt}}{C_{acid}} \quad \dots (XIII.76)$$

This equation, generally known as Henderson equation, shows that pH of the buffer is governed by salt-acid ratio and the ionisation constant of the acid.

For a mixture of a weak base and its salt, similar treatment would show

$$C_{OH^-} = K_b \cdot \frac{C_{base}}{C_{salt}}$$

$$\text{or} \quad pOH = pK_b + \log \frac{C_{salt}}{C_{base}} \quad \dots (XIII.77)$$

The buffering capacity is best when the acid and the salt are present in equal concentrations in the mixture, so that

$$pH = pK_a$$

Thus a sodium acetate-acetic acid buffer's capacity is maximum when equimolecular concentrations are taken in their mixture ; the pH becomes 4.74 (for $K_a = 1.82 \times 10^{-5}$).

When the ratio salt/acid is varied, the buffer will have a different pH, but not far away from the value of pK_a . For example, if acid : salt = 1 : 4,

$$pH = pK_a + \log 4 = pK_a + 0.60$$

But if the ratio acid to salt be 4 : 1, then

$$pH = pK_a + \log 1/4 = pK_a - 0.60$$

The maximum variation in the acid : salt ratio allowed is 1 : 10 or 10 : 1. The limiting values of the buffer pH then are

$$pH = pK_a + \log \frac{1}{10} = pK_a - 1 \text{ and } pH = pK_a + \log 10 = pK_a + 1 ;$$

i.e., $pH = pK_a \pm 1$.

In other words, the acetate-acetic acid buffer is suitable in the pH range 4.74 + 1 and 4.74 - 1, i.e., 5.74 - 3.74.

In expressing the pH of a buffer solution (equations XIII.76 and 77), the concentration terms instead of activities have been used. But when greater accuracy is demanded, the expression should be

$$a_{H^+} = K_a \cdot \frac{a_{HA}}{a_{A^-}}$$

or

$$pH = pK_a + \log \frac{a_{salt}}{a_{acid}}$$

$$= pK_a + \log \frac{C_s}{C_a} + \log \frac{f_{A^-}}{f_{HA}}$$

or

$$pH = pK_a + \log \frac{C_{salt}}{C_{acid}} + \log f_{A^-} \quad [\because f_{HA} = 1]$$

or

$$pH = pK_a + \log \frac{C_{salt}}{C_{acid}} - 0.505 z_A^2 \sqrt{i}$$

(from Debye-Hückel)

... (XIII.78)

In the laboratory buffers are extensively used. In analysis different precipitations are carried out in specific pH-ranges for which buffering is required, for example, in precipitation of phosphates or their separations. Buffers are required in pH-determinations by colorimetric method, as also in standardisation of glass electrodes and other e.m.f. measurements. In the industrial chemical processes, various operations are pH-controlled, e.g., electrodeposition of metals, tanning of leather, brewing of alcohols, manufacture of paper, baking, etc. The pH of the blood of normal human being is 7.4, and in internal applications of fluid etc. similar buffering is needed, in the study of soils also pH control is essential.

Some of the common buffers used in the laboratory with their pH-ranges are given below :

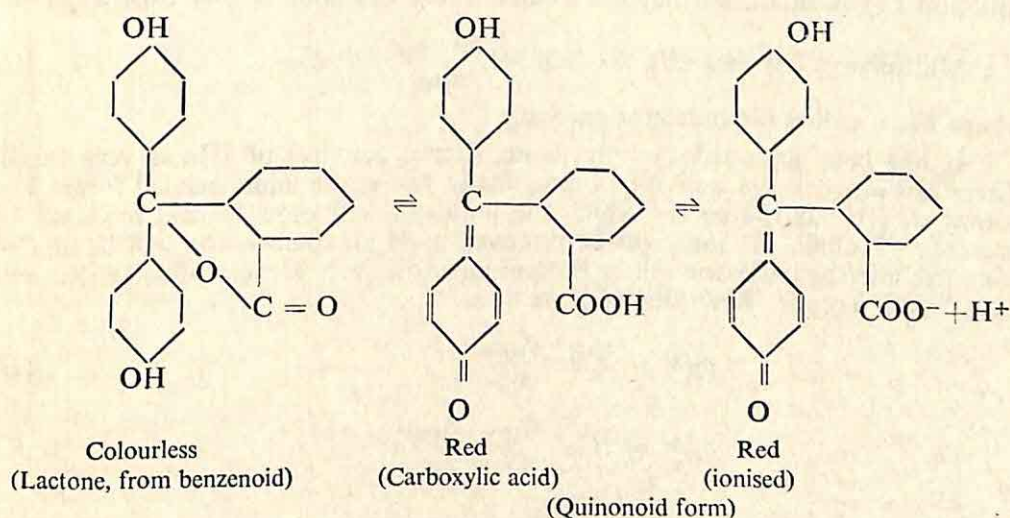
Buffer solutions	pH-range
1. Phthalic acid and pot. acid. phthalate	2.2 — 3.8
2. Acetic acid and Na-acetate	3.7 — 5.57
3. Pot-acid phthalate and dipotassium phthalate	4.0 — 6.2
4. Na_2HPO_4 and NaH_2PO_4	5.9 — 8.0
5. Boric acid and borax	6.8 — 9.2
6. Borax and NaOH	9.2 — 11.0

XIII.29. Indicators. The acid-base or neutralisation indicators are substances which exhibit different colours according to the H^+ ion concentration (or pH) of the solution to which they are added. It is therefore possible to obtain an idea of the pH of a given solution by adding a little of a suitable indicator to the same. Furthermore, if an indicator is present during the progress of titration of an alkali with an acid, the colour change of the indicator reveals the equivalence point of

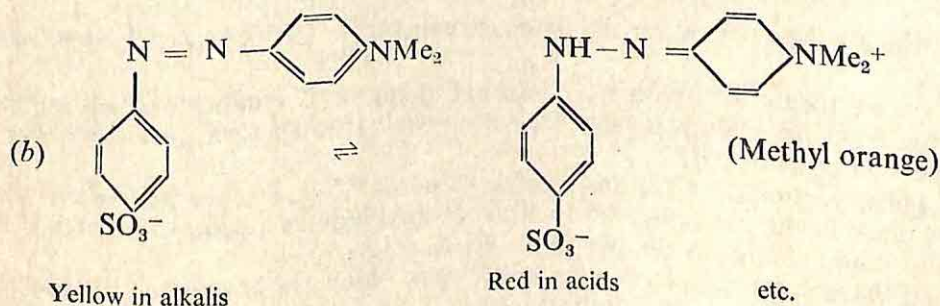
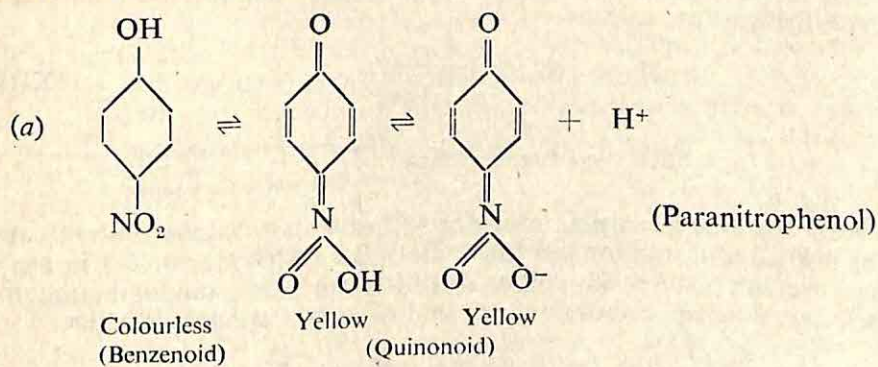
the titration. Most of the indicators have a predominantly "acid colour" and a predominantly "alkaline colour" in lower and higher ranges of pH. Different indicators undergo this change in colour from one to the other in different pH-ranges. For a given acid-base titration we can therefore select the indicator which would show a colour change close to the equivalence point of that reaction.

Indicators are either very weak organic acids or bases and these must exist in two tautomeric forms. One of the tautomers is in the non-electrolytic form and does not ionise but the other is an electrolyte and hence ionisable. The colours of the two tautomeric forms are different. The colour of the ion is the same as that of the tautomer from which it is produced.

For example, the commonly used indicator, phenolphthalein exists as follows :

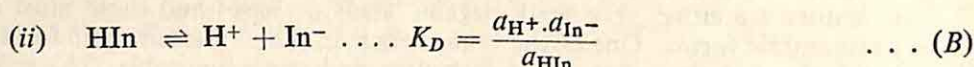
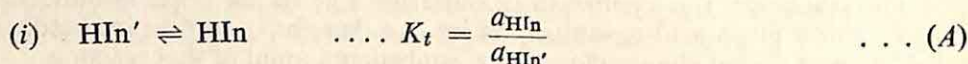


To cite other instances of indicators :



Let us now consider an indicator acid like phenolphthalein. Suppose HIn' be the non-ionisable tautomeric form and HIn be the ionisable form, while In⁻

represents the indicator ion. The colour of HIn and In^- is the same but different from that of HIn' . In aqueous solution there would exist two equilibria.



In acid solutions, the dissociation will be repressed, the whole of the indicator shall remain in undissociated form *i.e.*, as HIn' and HIn , which have different colours. The indicators will be applicable only if the equilibrium constant K_t of equation (A) is small, so that the undissociated indicator mostly exist as HIn' .

$$\text{Multiplying (A) and (B), } K_t \cdot K_D = \frac{a_{\text{H}^+} \cdot a_{\text{In}^-}}{a_{\text{HIn}'}} = K_{in} \quad \dots (C)$$

where K_{in} is called the indicator constant.

It has been assumed that the conc. (hence activity) of HIn is very small. Therefore $a_{\text{HIn}'}$ is the activity of practically the entire undissociated form. The colour of HIn' is the colour which the indicator will show in acid medium. In presence of alkali, H^+ ions will be removed as H_2O , dissociation will be almost complete and the indicator will be present mostly as In^- . Hence indicator ion shall have 'alkali' colour. Rewriting (C), we have

$$a_{\text{H}^+} = K_{in} \cdot \frac{a_{\text{HIn}'}}{a_{\text{In}^-}} \quad \dots (D)$$

$$\text{i.e.} \quad a_{\text{H}^+} = K_{in} \frac{C_{\text{HIn}'}}{C_{\text{In}^-}} \cdot \frac{f_{\text{HIn}'}}{f_{\text{In}^-}}$$

$$\text{or} \quad \text{pH} = \text{p}K_{in} + \log \frac{C_{\text{In}^-}}{C_{\text{HIn}'}} + \log f_{\text{In}^-} \quad (f_{\text{HIn}'} = 1) \quad \dots (E)$$

$\log f_{\text{In}^-}$ may be evaluated with Debye Hückel Law, but for most purposes, it is small and disregarded, so that

$$\text{pH} = \text{p}K_{in} + \log \frac{C_{\text{In}^-}}{C_{\text{HIn}'}} \quad \dots (\text{XIII.79})$$

$$\text{or} \quad \text{pH} = \text{p}K_{in} + \log \frac{C_{\text{ionised form with alkaline colour}}}{C_{\text{non-ionised form with acid colour}}}$$

It is seen that at a given pH, indicator will exist in a definite ratio of concentrations of ionised and non-ionised form. Both the forms are present in any pH. But human eye can discern the colour distinctly when one predominates. It has been found that the acid colour, namely that of HIn' , is detected when

$$\frac{C_{\text{HIn}'}}{C_{\text{In}^-}} \geq 10, \text{ i.e., when } \text{pH} = \text{p}K_{in} - 1.$$

And the alkaline colour can be detected when $\frac{C_{\text{In}^-}}{C_{\text{HIn}'}} \geq 10, \text{ i.e., } \text{pH} = \text{p}K_{in} + 1.$

As we titrate acid with base, the pH changes. The indicators will appear to change from one colour to another within the pH range $(\text{p}K_{in} + 1)$ to $(\text{p}K_{in} - 1)$, within two units of pH.

Thus, phenolphthalein has a $\text{p}K_{in}$ value of 9.6 and hence its colour change takes place in the pH range 8.6 to 10.6. Methyl red has a $\text{p}K_{in}$ value of 5.1, so its colour would change in the pH-range 4.1 to 6.1.

In the case of indicators which are weak bases, we have again the tautomers $\text{In}'\text{OH}$ and InOH and the equilibria are :



InOH and In^+ have the same colour but different from that of In'OH . To be useful as indicator, K_t must be small, the undissociated form shall mostly be In'OH . As before, we have,

$$K_{in} = \frac{a_{\text{In}^+} \cdot a_{\text{OH}^-}}{a_{\text{In'OH}}} \quad \text{or} \quad a_{\text{OH}^-} = K_{in} \frac{a_{\text{In'OH}}}{a_{\text{In}^+}}$$

$$\therefore a_{\text{H}^+} = \frac{K_w}{K_{in}} \cdot \frac{a_{\text{In}^+}}{a_{\text{In'OH}}} \approx \bar{K} \cdot \frac{C_{\text{In}^+}}{C_{\text{In'OH}}} \quad (\text{assuming activity coefficients as unity.})$$

$$\text{or} \quad \text{pH} = \text{p}\bar{K} + \log \frac{C_{\text{In'OH}}}{C_{\text{In}^+}} \quad \dots \text{(XIII.80)}$$

where $\bar{K} = K_w / K_{in}$

Some of the commonly used acid-base indicators with the pH-ranges for their colour-change are listed below.

TABLE : ACID-BASE INDICATORS

Indicator	$\text{p}K_{in}$	Colour-change acid-alkali	pH-range
Bromo-phenol blue	4.0	yellow-blue	2.8— 4.6
Methyl orange	3.7	red-yellow	3.1— 4.4
Bromo cresol-green	4.7	yellow-blue	3.8— 5.4
Methyl red	5.1	red-yellow	4.2— 6.3
Chlorophenol red	6.0	yellow-red	4.8— 6.4
<i>p</i> -nitrophenol	7.1	colourless-yellow	5.6— 7.6
Bromo-cresol purple	6.3	yellow-purple	5.2— 6.8
Bromo-thymol blue	7.0	yellow-blue	6.0— 7.6
Phenol red	7.9	yellow-red	6.8— 8.4
Cresol red (base)	8.3	yellow-red	7.2— 8.8
Thymol blue (base)	8.9	yellow-blue	8.2— 9.6
Phenolphthalein	9.6	colourless-red	8.3—10.0
Thymolphthalein	9.2	colourless-blue	8.3—10.5

Choice of Indicators. When equivalent amounts of a strong acid (say HCl) and a strong base (say KOH) are mixed, the resulting solution has a pH near about 7.0 and any indicator may be used in such neutralisation titrations. On the other hand, if to a weak acid solution an equivalent amount of a strong base be added, the resulting salt in solution suffers hydrolysis and the solution is alkaline having a pH above 7.0. Hence in a titration of a weak acid and a strong base, indicators whose colour-change takes place in a higher range, such as phenolphthalein or thymol-blue should be used. In titrating a strong acid with a weak-base (say HCl acid with Na_2CO_3 soln), the resulting salt suffers hydrolysis and the solution becomes acidic even when equivalent amounts are added. The indicators like methyl orange, methyl red etc. whose colour-change takes place in the acidic pH-range would prove satisfactory. In titration of weak acids with weak bases, none of the indicators are very satisfactory.

The statement just made may be more clearly understood from a titration curve with variation in pH of the solution.

Suppose 100 c.c. of 0.1 *N* HCl are being titrated with 0.1 *N* NaOH . Assuming complete dissociation and activities being the same as concentrations, the H^+ -ion concentration at any stage of titration is equal to the amount of HCl remaining unneutralised. The pH-values may then be calculated as.

c.c. of NaOH added	% HCl unneutralised	C_{H^+}	pH
nil	100	10^{-1}	1.0
50	50	5×10^{-2}	1.3
99.9	0.1	10^{-4}	4.0
100.0	0.0	10^{-7}	7.0
100.1	Excess alkali	10^{-10}	10.0

This shows that when 0.1 c.c. of titre only remains to be added to reach equivalence point, pH was 4.0. With another 0.2 c.c., the pH has sharply jumped to pH = 10. This is illustrated in Fig. XIII.14(a).

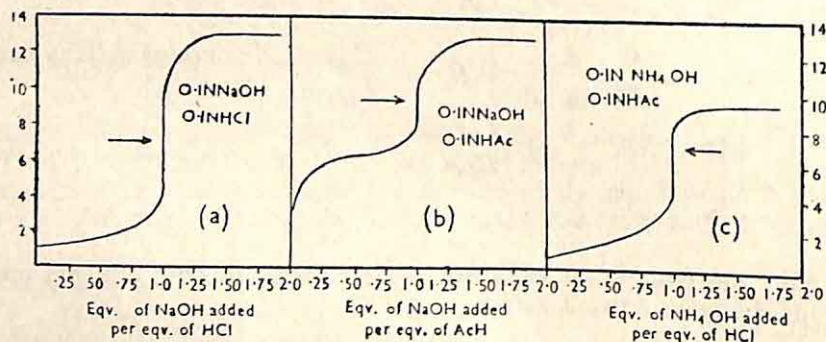


FIG. XIII.14 Neutralisation curves (a) 0.1 *N* HCl and 0.1 *N* NaOH, (b) 0.1 *N* AcH and 0.1 *N* NaOH (c) 0.1 *N* NH₄OH and 0.1 *N* HCl

If instead of HCl, 0.1 *N* acetic acid is titrated with 0.1 *N* NaOH, the titration curve Fig. XIII.14(b) is obtained. Since the salt NaAc hydrolyses, the pH-jump takes place from approximately 7.0 to 10.0, where the equivalence point is reached. The pH-values at different stages are calculated with Henderson equation (XIII.76). In this titration necessarily phenolphthalein is used as indicator as its pH range for colour-change is about 9.0.

Likewise in titrating 0.1 *N* HCl with 0.1 *N* NH₄OH, the pH of the solution, calculated with Henderson equation, shows a steep rise from pH = 4.0 to pH = 7.0 when the equivalence point is reached (Fig. XIII.14(c)). Methyl orange is thus a suitable indicator in this titration.

XIII.30. Determination of pH of Solution by Colorimetric Method. The first step is to have an idea of the approximate pH of the given solution. This is done with the help of a universal multirange B.D.H. indicator. This is indeed a mixture of several indicators. The B.D.H. universal indicator when added to the solution develops a colour which is matched against colour charts supplied by the manufacturers. This enables one to have an approximate estimate of the pH-range of the solution under test.

Suppose the approximate pH of the solution is found to be in the range 6.0—7.0. A series of buffer solutions are then prepared in that range, say from pH = 5.0 to pH = 7.6 differing successively in pH by about 0.2. In this case, primary-secondary phosphate buffers will be suitable. Ten c.c. of each of these buffer solutions are taken in clean test tubes and to each 0.5 c.c. of an indicator soln suitable for that pH-range is added (here Bromothymol blue (B.T.B.) indicator would be suitable). The buffer solutions will have gradually changing shades of colour. In another test tube of same dimensions, 10 c.c. of the experimental solution is taken to which 0.5 c.c. of the same indicator is added. The colour produced is then compared with the coloured buffer solutions. When a complete match is obtained, the test solution and the corresponding buffer solution will have the same pH. In this way, pH-value of the solution accurate up to 0.2 pH unit can be determined. A more accurate value can be obtained if buffers could be prepared differing by 0.1 pH unit. Often Lovibond or Hellige comparator is used for matching the colours. Series of permanent glass colour standards for different pH-ranges are supplied, fitted in a disc. Solutions with indicators are taken in small rectangular cells and matched with the coloured glass standards to obtain the pH-value. Indicators to be used for such comparator methods are also to be obtained from specific manufacturers. Details may be found in a practical text book.

POLARISATION : OVERVOLTAGE

XIII.31. Polarisation. In a voltaic cell, electric energy is produced at the cost of chemical reactions. From thermodynamic considerations we know that the amount of electrical energy produced under *reversible* conditions is equal to the free energy decrease. But if the electrode processes are irreversible, the electrical energy output will be less than the decrease in free energy ; a portion of the free energy will be dissipated as heat.

The opposite non-spontaneous process, namely the chemical reaction at the cost of electric energy, can be effected by passing electricity under a suitable applied potential through a cell where the same chemical transformation could occur. This is *electrolysis* and would increase the free energy. Under reversible conditions, the free energy changes, though opposite in sign, would be equal in magnitude in the two opposite transformations.

But in most of our practical applications, which are generally rapid, the conditions of reversibility are not observed. The energy required to carry out the chemical process is that necessary for the thermodynamically reversible change plus an extra amount to compensate for the irreversibility. It is thus easily realised that under irreversible conditions, the applied potential needed for electrolysis would be greater than the reversible e.m.f. of the corresponding voltaic cell. The extra voltage required over the theoretical for electrolysis is called the *polarisation voltage*, since the phenomenon is known as *polarisation*. The cell is said to be polarised.

XIII.32. Decomposition Potential. Suppose we attempt decomposition of an 1M H_2SO_4 solution by dipping two smooth pt-electrodes in it. An arrangement as in Fig. XIII.15(a) may be made in which the pt-electrodes *A* and *B* are inserted in the acid solution. The potential is applied from a battery *X* through a variable resistance in the acid solution. The potential can be varied by moving the sliding contact *D*. A milliammeter *C* is inserted in the circuit and also a key *E*. The voltmeter *V* is connected to the two electrodes to measure the potential between the two at any moment.

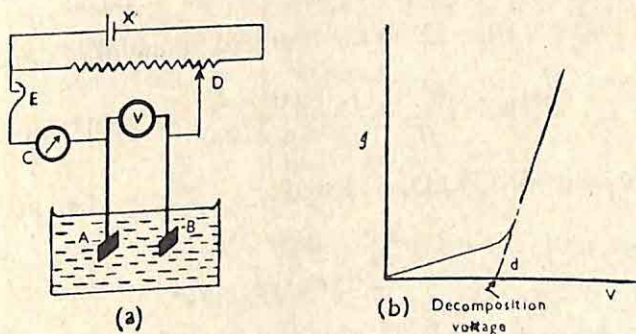


FIG. XIII.15 (a) Decomposition potential measurement (b) Plot of current vs. applied potential

To begin with, let a small voltage, say 0.5 volts, be applied. The ammeter *C* will first show an appreciable current is flowing. But the current soon falls and is gradually reduced to almost zero. The applied voltage is then slowly increased but the current strength increases very slightly until when the applied voltage reaches a certain value the current suddenly increases rapidly with increase in applied voltage. At the point where a sudden increase in current takes place, bubbles of gas also begin to be evolved at the electrodes, i.e., electrolysis or decomposition starts. If the current is plotted against voltage, a curve as shown in Fig. XIII.15(b) is obtained. The decomposition starts when the voltage is raised to the point, *d*. This voltage is called the *decomposition potential*. The decomposition potential of an electrolyte may then be defined as the minimum potential to be applied in order to bring about continuous electrolysis.

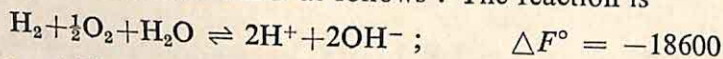
After the voltage has been applied for some time, if the circuit is broken, it is found that the reading of the voltmeter V remains steady for sometime and then falls quite rapidly to zero. It means that the electrolytic cell is behaving as a source of current. It is said to be exercising a *back* or *polarisation* e.m.f. in a direction opposite to that of the applied potential. The back e.m.f. is due to the fact that during electrolysis, oxygen and hydrogen gases accumulate at the pt-anode and cathode respectively. The two inert electrodes have thus been converted into oxygen and hydrogen electrodes. The H_2-O_2 voltaic cell so formed has an e.m.f. opposite to that of the external applied voltage. A current from this cell will be obtained until the accumulated gases are used up or diffuse away. The back e.m.f. exists even when external potential is applied. That is why continuous electrolysis is not observed at low applied potentials as seen in Fig. XIII.15(b). So it is found that as a result of electrolysis, even inert electrodes are converted into active ones to yield current.

With smooth pt-electrodes, the decomposition potential in the case of H_2SO_4 has been experimentally found to be 1.7 volts. Although the electrolyte is H_2SO_4 , and the electricity is conveyed by H^+ and SO_4^{--} ions, the chemical change is really the decomposition of water. This is proved from the fact when different alkalis and other oxyacids are taken as electrolytes—all yield H_2 and O_2 gases—the same decomposition voltage is observed (vide Table below); whereas the decomposition voltage of HBr is 0.94 volts and of HCl 1.31 volts.

TABLE : DECOMPOSITION VOLTAGES WITH SMOOTH PT-ELECTRODES

<i>Electrolyte</i>	<i>Decomp-Pot.</i>	<i>Electrolyte</i>	<i>Decomp-Pot.</i>
H_2SO_4	1.67 volts	$HClO_4$	1.64 volts
HNO_3	1.69	$NaOH$	1.69
H_3PO_4	1.70	KOH	1.67
$CH_2Cl.COOH$	1.72	NH_4OH	1.74

For a voltaic cell with reversible H_2-O_2 electrodes, we can calculate thermodynamically the reversible e.m.f. as follows : The reaction is



Since $\Delta F^\circ = -nFE^\circ$, where E° is the standard potential of the cell,

$$E^\circ = \frac{\Delta F^\circ}{-2f} = \frac{-18600 \times 4.2}{-2 \times 96500} = 0.403 \text{ volts.}$$

When the electrolyte used is H_2SO_4 or a similar substitute, then, at $25^\circ C$,

$$\begin{aligned} E &= E^\circ - \frac{RT}{2f} \ln \frac{a_{H^+}^2 \cdot a_{OH^-}}{a_{H_2} \cdot a_{O_2} \cdot a_{H_2O}} \\ &= E^\circ - \frac{RT}{f} \ln a_{H^+} \cdot a_{OH^-} = 0.403 - 0.059 \log a_{H^+} \cdot a_{OH^-} \end{aligned}$$

i.e.,

$$E = 0.403 - 0.059 \log (1 \times 10^{-14}) = 1.23 \text{ volts}$$

In other words, the reversible potential of any cell in which the chemical process is the electrolysis of water is 1.23 volts. This potential is independent of the nature and concentration of electrolyte used.

It is thus seen that with smooth pt-electrodes the polarisation voltage of electrolyte H_2SO_4 , or the like, is $1.7 - 1.23 = 0.47$ volts. It is not possible to say definitely from this observation alone whether the polarisation potential is associated with only one electrode or with both the electrodes.

XIII.33. Concentration Polarisation and Overvoltage. The polarisation during electrolysis is of two types, namely (a) *Concentration polarisation* and (b) *Overvoltage*. Both of them may arise simultaneously.

(a) *Concentration Polarisation.* As a result of electrolysis ions are discharged on the electrodes and as such changes in the concentration of ions in the immediate vicinity of the electrodes occur. This is particularly noticeable when the ions are slow-moving. In effect, a concentration cell within is created whose e.m.f. may act in opposition to the applied e.m.f. This is concentration polarisation.

Let us consider the variation in potential at the cathode during electrolytic deposition. The initial concentration of the ion when electrolysis starts is, suppose C_i , for a bivalent ion, (say Ni^{++} being discharged,) the electrode potential is

$$\xi = \xi^\circ - \frac{RT}{2f} \ln C_i = \xi^\circ - \frac{0.059}{2} \log C_i$$

Suppose the concentration is reduced thousand fold due to electrolysis, then the electrode potential would be

$$\begin{aligned} \xi' &= \xi^\circ - \frac{0.059}{2} \log (C_i \times 10^{-3}) \\ &= \xi^\circ - \frac{0.059}{2} \log C_i + 3 \times \frac{.059}{2} \\ &= \xi + 0.087. \end{aligned}$$

that is, the electrode potential would change by 0.087 volts.

The concentration polarisation is usually small and even this can be practically eliminated by vigorous stirring of the electrolyte. Increase of temperature also reduces concentration polarisation due to increased thermal diffusion.

(b) *Overvoltage.* The overvoltage is a polarisation potential associated with the processes occurring at the electrode surface. This effect is particularly important when the product of electrolysis is a gaseous one. An irreversibility is introduced in the processes at the electrode due to slowness at some stage. Usually two or three stages are involved in the discharge of the product on the electrode. First the ions are deposited on the electrode and neutralised, the neutral atoms are then deposited or rendered into molecules, if polyatomic; and finally, the molecules escape, if gaseous, in the form of bubbles. Let us explain this with the liberation of hydrogen at a smooth Pt-cathode.

The steps associated with H_2 -evolution are

- (a) $\text{H}^+ + e \rightleftharpoons \text{H (atom)}$
- (b) $2\text{H} \rightleftharpoons \text{H}_2 \text{ (adsorbed)}$
- (c) $\text{H}_2 \text{ (adsorbed)} \rightleftharpoons \text{H}_2 \text{ (gas)}$

The processes at (a) and at (c) are quite rapid and these equilibria are easily attained. But as for the process at (b), the formation of hydrogen molecule from atomic hydrogen is a slow process and the consequent equilibrium is only arrived at with difficulty. For a given H^+ ion concentration in the solution, the electrode potential will be determined by H^+ ion concentration and hence by atomic hydrogen on the electrode. The atomic hydrogen concentration is again dependent on gaseous hydrogen molecules. As eqm (b) is not readily attained, the electrode cannot act as reversible H_2 -electrode. Because of the slowness of the reaction $2\text{H} \rightarrow \text{H}_2$, a relatively high concentration of atomic hydrogen on the electrode is necessary before the rate of reaction $2\text{H} \rightarrow \text{H}_2$ would equal the rate at which H^+ ions are discharged by process (a). This high concentration of atomic hydrogen is much greater than required by eqm envisaged in process (a). The result is that due to high concentration of atomic hydrogen, and hence of H^+ ions, the electrode potential is much greater than that of the reversible hydrogen electrode. This excess e.m.f. is the overvoltage of hydrogen on that electrode. If the electrode be such which catalyse the process (b), i.e., the hydrogen atoms are catalysed to form H_2 -molecules, then the overvoltage can be considerably reduced. In fact, if platinised platinum be used, the overvoltage is practically absent.

This is only one of many proposed to explain overvoltage.

The overvoltage at the anode or cathode depends on the following :

- (a) the nature and the physical state of the electrode employed.
- (b) the physical state of the substance deposited. If it is a metal the overvoltage is usually small, but for a gas the overvoltage is higher.
- (c) the current density employed and the temperature. In the table here we enlist the hydrogen overvoltage in $2N$ H_2SO_4 for the beginning of formation of bubbles.

TABLE : H_2 -OVERVOLTAGE IN $2N$ H_2SO_4 AT ROOM TEMP.

Electrode	Overvoltage	Electrode	Overvoltage
Pt (platinised)	0.00	Ni	0.21
Pt (smooth)	0.09	Cd	0.48
Au	0.02	Sn	0.53
Ag	0.15	Pb	0.64
Cu	0.23	Zn	0.70
Fe	0.08	Hg	0.78

Measurement of Overvoltage. An arrangement as in Fig. XIII.16 is made for direct measurement of overvoltage at an electrode during electrolysis. This arrangement is similar to that employed for measuring the decomposition potential. The electrodes (A+B) are kept partially immersed in the solution electrolysed which is continuously stirred with stirrer S , to avoid concentration polarisation. The solution end of a reference electrode, say calomel half-cell, is also placed in the solution and kept very close to the electrode under test. The electrode (say A) and the reference electrode constitute a cell and these are connected to a potentiometer. The e.m.f. is recorded from

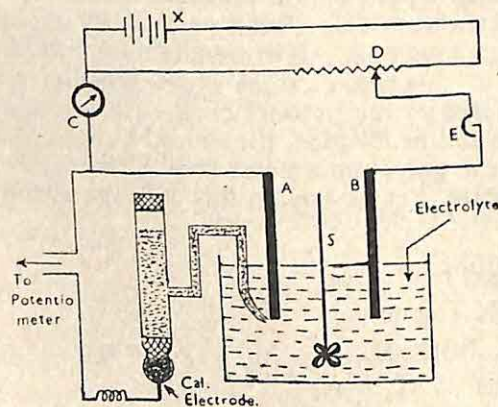


FIG. XIII.16

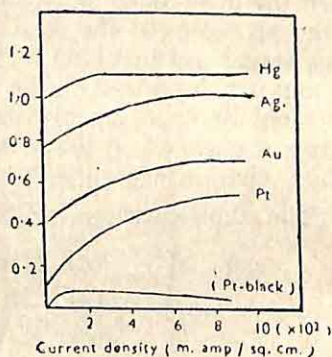
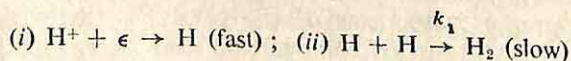


FIG. XIII.17

the potentiometer and by subtracting the potential of the reference electrode from the e.m.f. measured, the potential of the electrode (A) concerned is obtained. The reversible electrode potential of A being known, the excess potential of A during electrolysis is found out which is the overvoltage. The experiment is repeated with different currents used for electrolysis. The overvoltages with different current densities are thus obtained. The area of the electrodes which is inside the solution is carefully measured, the current strength is known from the milliammeter, hence current density is known.

A relation for the variation of overvoltage (V) with current density (I) may be easily derived. Consider the two primary processes at the cathode :



The cathode reaction is governed by process (ii).

We know,
$$\xi = \xi^0 - \frac{RT}{f} \ln \frac{C_H}{C_{H^+}},$$

where C_{H^+} = conc. of H^+ ions in the solution and C_H = conc. of H-atoms measured per unit area of the cathode surface. Again, the rate of formation of H_2 -molecules per unit area of the surface is the current density. Hence $I = k_1 C_H^2$ or $C_H = \sqrt{I/k_1}$

$$\therefore \xi = \xi^\circ - \frac{RT}{f} \ln \frac{\sqrt{I/k_1}}{C_{H^+}}$$

If ξ_a denote the actual eqm. potential, so that $V = \xi - \xi_a$.

$$\therefore V = \left[\xi^\circ - \xi_a - \frac{RT}{f} \ln \frac{1}{\sqrt{K_1} C_{H^+}} \right] - \left[\frac{2.303 RT}{2f} \right] \log_{10} I$$

$$= -a - b \log_{10} I$$

where $-a$ and b replace the quantities within the brackets.

The overvoltage $-V = a + b \log_{10} I$

. . . (XIII.81)

It is therefore expected that the plot of V against $\log_{10} I$ would be linear. This has been realised in the case of hydrogen overvoltage to some extent (Fig. XIII.17).

XIII.34. Processes at the Cathode : Metal Deposition. There are some interesting aspects of the processes occurring at the cathode during electrolysis.

(i) The transport of current through the solution depends on the speed and concentration of the ions, but the discharge of the ions depends on the deposition potential of the ion in that solution. These two phenomena are independent. It is thus possible that the ion discharged at an electrode is different from the ion which is primarily responsible for conducting the electricity.

For instance, in the electrolysis of an acid solution of $AgNO_3$ between Pt-electrodes, the current towards the cathode is largely transported by H^+ ions and to some extent by silver ions and yet only Ag^+ ions are discharged at the cathode and not H^+ ions. On the other hand the current towards the anode is conveyed almost wholly by NO_3^- ions and yet the OH^- ions are discharged to yield oxygen gas.

(ii) It has already been stated that in the deposition of metals there is very little overvoltage needed. That is, metals are deposited practically at their own reversible potentials. When aqueous solutions of metallic salts are electrolysed, metal ions as well as hydrogen ions are present to be discharged on the cathode. There indeed would be a competition between the two for discharge. In such a case, the ion which has a higher discharge potential under a given set of conditions will be liberated at the cathode during electrolysis.

For instance, take the case of neutral $AgNO_3$ solution ($a = 1$), the reversible deposition potential for $Ag = +0.79$ volts, the deposition potential of hydrogen is $= +(0.059 \log 10^{-7}) = -0.41$ volts. It is thus seen that the free energy decrease ($-n f \xi$) will be greater in the case of Ag -deposition than that in hydrogen deposition. Ag^+ ions will therefore have a greater tendency to be spontaneously deposited and that is why we observe silver plating out of the solution.

If the deposition potential of a metal is less than that of hydrogen, it is expected that hydrogen would be evolved at the cathode. But in computing the deposition potential of hydrogen not only its reversible potential but also the overvoltage of hydrogen on the cathode material must be taken into consideration. It is because of the appreciable hydrogen overvoltage that many metals are found to be deposited from aqueous solutions instead of hydrogen, although the decomposition potential of metal is less than that of the hydrogen.

To Illustrate : In a neutral solution,

the reversible deposition potential of Zn ($a = 1$) $= -0.76$

and that of hydrogen ($a = 10^{-7}$) $= -0.41$

Yet zinc is deposited on zinc cathode and not hydrogen because the actual deposition potential of hydrogen is its reversible potential (-0.41 volts) plus its overvoltage (-0.70 volts) i.e., -1.11 volts. This is much lower than that of zinc and hence zinc is deposited.

An outstanding application of this effect is found in Castner cell for caustic soda. The decomposition potential of sodium on a dilute sodium-mercury amalgam, (in which activity of sodium is low) is about -1.2 volts. The reversible deposition potential of hydrogen plus its overvoltage on mercury is about -1.4 volts. So, sodium is deposited on the mercury cathode and not hydrogen. But when the amalgam is led to the next chamber with iron cathode, the picture is different. Sodium has now a reversible potential of about -2.5 volts where as the deposition potential of hydrogen including overvoltage on iron is much less. Hence hydrogen is liberated there.

(iii) When ions of more than one metal are present in solution each ion will be liberated at its appropriate deposition potential. These deposition potentials are approximately their reversible discharge potentials, for metals are usually found to have no overvoltage. Thus, if a solution contains Zn^{++} and Ag^+ , both at unit activities (say), Ag^+ ions would be liberated first on a Ag -electrode when the cathode potential is -0.79 volts. If the Ag is practically wholly removed by electrolysis, the current will fall, the electrode may be replaced by zinc and the potential adjusted to that for deposition of zinc. In this way, electrolytic separation can be effected. In the electrolysis with a mixture of several salts, metals which have a lower oxidation potential will be deposited earlier than those which have a higher oxidation potential.

(iv) Sometimes simultaneous separation of two metals may be necessary, such as the electrolytic process of formation of brass by joint deposit of copper and zinc. In aqueous solution of the two salts having equal concentrations, their deposition potentials are widely different. Hence it is necessary to take these ions in such concentrations that their decomposition potentials may be equal. This is usually achieved by transforming these ions into their complexes, e.g., complex cyanides. The difference in their deposition potentials is thereby reduced and ultimately at a particular concentration of cyanide the decomposition potentials of the two are made equal and both are then deposited simultaneously.

Reference for further reading

1. Introduction to Electrochemistry—Glasstone
2. The principles of Electrochemistry—Mac Innes
3. The physical chemistry of Electrolytic solutions—Harned and Owen
4. Principles and application of Electrochemistry—Creighton and Koehler
5. Text book of Electrochemistry—Kortum and Bockris
6. Potentiometric titrations—Kolthoff
7. Hydrogen ions—Britton
8. Indicators—Kolthoff.

Problems

If necessary, in solving these problems, the standard essential data are to be taken from the tables given in the book. Unless otherwise stated, the temp. is to be taken as 25°C .

1. Write down the individual electrode reactions and also the total cell reaction for each of the following cells.

- (a) $\text{Pb} \mid \text{PbSO}_4(s), \text{SO}_4^{--} \parallel \text{Cu}^{++} \mid \text{Cu}$
- (b) $\text{Pb} \mid \text{H}_2\text{SO}_4 \mid \text{PbO}_2(\text{Pb})$
- (c) $\text{Zn} \mid \text{Zn}^{++} \mid \text{H}^+ \mid \text{H}_2(\text{Pt})$
- (d) $\text{Fe} \mid \text{Fe}^{++} \parallel \text{Fe}^{++} - \text{Fe}^{+++}(\text{Pt})$

2. Give the cell reactions of the following cells and calculate their standard e.m.f., using the table in this chapter, at 25°C .

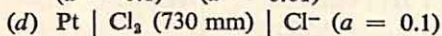
- (a) $\text{Hg} \mid \text{Hg}_2\text{Cl}_2(s) \mid \text{Cl}^- \parallel \text{Cu}^{++} \mid \text{Cu}$
- (b) $\text{Pt} \mid \text{Fe}^{++} - \text{Fe}^{+++} \parallel \text{Cl}^- \mid \text{AgCl}(s) \mid \text{Ag}$
- (c) $\text{Cu} \mid \text{Cu}^{++} \parallel \text{Pb}^{++} \mid \text{Pb}$.

3. Calculate the potentials of the following electrodes at 25°C .

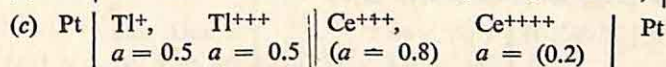
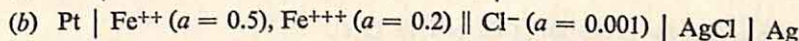
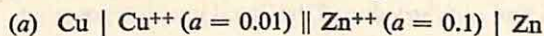
- (a) $\text{Ag} \mid \text{Ag}^+ (a = 10^{-5})$
- (b) $\text{Cu} \mid \text{Cu}^{++} (a = 0.2)$



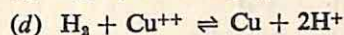
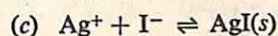
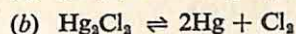
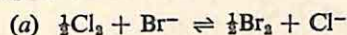
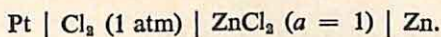
$$(a = 0.1) \quad (a = 0.01)$$



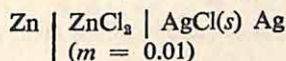
4. Compute the cell potentials of the following :



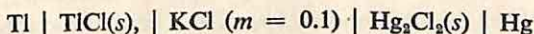
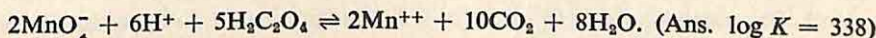
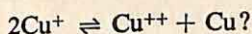
5. Construct electrochemical cells for the following reactions and then find out their standard free energy changes from their e.m.f.'s :

6. Calculate the e.m.f. of the cell and ΔF° of the cell reaction, for

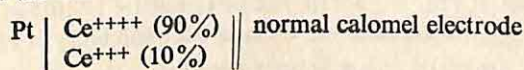
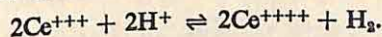
7. The potential of the cell,

is 1.16 volts. Show that mean ionic activity of the ZnCl_2 solution is about 0.71.

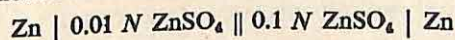
8. The e.m.f. of the cell

is 0.73 volts, and $dE/dT = 7.5 \times 10^{-4}$. What is the cell reaction? Calculate ΔH and ΔF for the reaction.9. Given $\xi^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = -1.51$, and $\xi^\circ_{\text{CO}_3/\text{oxalate}} = 0.49$; calculate the eqm constant of the reaction10. The oxidation potentials of $\text{Cu} \mid \text{Cu}^{2+}$ and $\text{Cu} \mid \text{Cu}^+$ are 0.337 and 0.530 volts. What is the equilibrium constant of the reactionIs it easier to oxidise copper to Cu^{2+} or Cu^+ ion state?

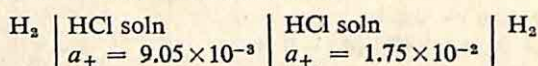
11. The e.m.f. of the cell

is 1.464 volts at 18°C . Calculate the value of the equilibrium constant of the reaction,

12. The electromotive force of the cell

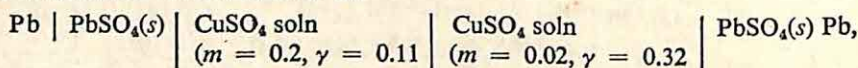
is 0.0275 volts. The ionic conductances $l_{\text{Zn}^{2+}} = 47$ and $l_{\text{SO}_4} = 70$. Calculate the ratio of ionic concentrations.13. The electrode potential $\text{Cu} \mid \text{Cu}^{2+} (1 \text{ M})$ is -0.62 volts. At what concentration of copper ions will this electrode potential be zero?14. If excess metallic iron be added to a solution containing $\text{N } \text{Cu}^{2+}$, calculate the approximate concentration of copper ions when equilibrium is established.15. Calculate the e.m.f. of a cell consisting of two copper plates dipping in 0.05 N and 0.005 N copper sulphate solutions. Neglect liquid junction potential.16. The e.m.f. of a cell formed by dipping two electrodes of a metal (X) in two solutions of its salt with concentrations 0.1 M and 0.01 M was observed to be 0.0295 volts at 25°C . What is the valency of the metal, if liquid junction potential has been eliminated?

17. The e.m.f. of the cell, with transference,



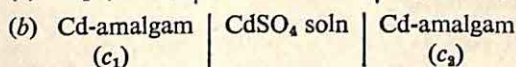
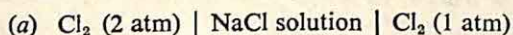
is found to be 0.028 volts at 25°C. Its e.m.f. without transference is 0.017 volts. What is the transport number of Cl^- ions. Also find out the value of the liquid junction potential.

18. Calculate the potential of the cell, at 25°C,



if transference number of Cu^{++} be 0.37.

19. Calculate the e.m.f. of the following cells at 20°C ;



$$\text{where } c_1 = 5.3 \times 10^{-5}, c_2 = 1.8 \times 10^{-3}$$

20. Explain

(i) Why nickel sulphide alone is precipitated when H_2S is passed into an aqueous solution containing Ni^{++} and Mn^{++} and dilute acetic acid (M/10).

(ii) Why zinc sulphide is insoluble in water but soluble in dilute HCl but mercury sulphide is insoluble in both water and in dil HCl.

(iii) Why silver chloride dissolves in ammonia but not in HCl, whereas barium phosphate dissolves in HCl but not in ammonia.

21. The solubility products of AgCl and AgI are 10^{-10} and 10^{-8} respectively. What will be the effect of

- adding KCl soln to a saturated solution of AgCl ,
- shaking up solid AgCl with a solution of KI ,
- shaking up solid AgI with HCl solution?

22. The solubility of AgCl in water is 1.50 mgm/litre at 20°C. What will be its solubility in $1 \times 10^{-2} M$ KCl solution?

23. The solubility product of Magnesium hydroxide is 3.4×10^{-11} . Calculate its solubility in gms/litre.

24. At 25°C, the solubility product of AgBrO_3 is 5.8×10^{-5} . Calculate its solubility in pure water and in 0.01 M KBrO_3 , using Debye-Huckel limiting law.

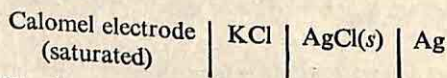
25. The solubility product of PbI_2 is 7.5×10^{-9} at 15°C and 1.4×10^{-8} at 25°C. Show that the molar heat of solution of PbI_2 is 10,600 calories. Calculate the solubility of PbI_2 at 35°C.

26. At 25°C the activity product $L_a = 7 \times 10^{-9}$ for MgF_2 . Calculate its solubility in moles/litre in water and in 0.01 M NaF .
 (Ans. 1.2×10^{-3} , 7×10^{-5}).

27. At 18°C, the specific conductance of water saturated with CaF_2 is 3.86×10^{-5} . Show that its solubility is 1.48×10^{-2} gms/litre. Calculate its solubility product.

Given $l_+ = 51$, $l_- = 47$, and the specific conductance of water used, 1.5×10^{-6} .

28. The e.m.f. of the cell



was found to be 0.269 volts at 25°C. What is the solubility of silver chloride? (Given $\xi^\circ_{\text{Cal}} = 0.2415$ and $\xi^\circ_{\text{Ag}/\text{Ag}^+} = 0.7978$ volts).

29. Calculate H^+ , and PO_4^{---} concentrations in a 0.01 molar solution of phosphoric acid at 25°C. Use K_a values from the tables.

30. Find out the degree of dissociation and pH of a 0.01 molar solution of phenylacetic acid at 25°C, ($K_a = 4.8 \times 10^{-5}$).

31. A solution which is 0.05 M in respect of benzoic acid and 0.1 molar in sodium benzoate, has a pH = 4.50. Find the dissociation constant of the acid.

32. Calculate the ionic product of water from the e.m.f. of the following cells at 25°C;

(a) (Pt)-H₂ (1 atm) | KOH (0.01 *m*) || KCl (0.01 *m*) | AgCl(s) | Ag; e.m.f. = 1.0503 volts.

(b) (Pt)-H₂ (1 atm) | HCl (*a* = 1) | AgCl(s) | Ag; e.m.f. = 0.2224 volts.

Assume $\gamma_{\text{Cl}^-} = \gamma_{\text{OH}^-}$.

33. At 25°C, the e.m.f. of the cell

Glass electrode | buffer || calomel electrode

was found to be 0.0232 volts, when buffer pH was 2.5. The e.m.f. increased to 0.1120 volts when an unknown buffer is used. What is the pH of the second buffer? What would be the e.m.f. if a buffer of pH = 6.00 were used?

34. Calculate (using standard values of dissociation constants),

(a) the degree of hydrolysis of (i) 0.01 molar and 0.001 molar Na₂CO₃ solutions and (ii) 0.1 molar KCN solution at 25°C

(b) the hydrolytic constants of (i) ammonium carbonate and (ii) disodium hydrogen phosphate.

35. At 25°C and at a dilution of 32 litres, the eqv. conductance of ortho-toluidine hydrochloride is 98.5 and that of HCl at the same concentration is 383. On adding successive quantities of orthotoluidine to the solution of the salt, the eqv. conductance could be reduced to 89.7 but no further. Find out the degree of hydrolysis and the hydrolytic constant.

36. A solution of 12.95 gm of aniline hydrochloride in 100 c.c. of 0.01 *N* HCl is brought into equilibrium with 100 c.c. of benzene. The amount of aniline in benzene layer was estimated to be 0.1 gm. What is the hydrolysis constant of aniline hydrochloride, if partition coefficient of aniline between benzene and water is 10.

37. The overvoltage of H₂ on zinc is 0.72 volt when current density is 1 ma/cm². What will be the decomposition potential of hydrogen on this electrode when the solution has a pH = 3?

38. The overvoltage of H₂ on Fe is 0.40 volts at a current density of 1 ma/cm². In a solution containing Fe⁺⁺ ions (*a* = 1), what will be lowest pH for which deposition of Fe would be possible without 'gassing'?

39. Calculate pH of the solutions:

(i) 0.05 molal lactic acid and 0.122 molal Na-lactate ($K_a = 1.37 \times 10^{-4}$)

(ii) 0.1 molal ammonia and 0.24 molal NH₄Cl ($K_b = 1.8 \times 10^{-5}$)

40. What will be the pH of the solution obtained by mixing 500 c.c. of 0.1 *M* NaH₂PO₄ and 100 c.c. of 0.1 *N* NaOH. Given $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$.

41. Show that the buffer capacity (β) of a buffer prepared from a weak acid is maximum at the half-neutralisation point.

Let '*a*' and '*b*' be the conc. of acid and alkali mixed; $a > b$. The conc. of salt $C_s = b$, and final conc. of acid $C_a = a - b$. From Henderson eqn.;

$$\text{pH} = \text{p}K_a + \log \frac{C_s}{C_a} = \text{p}K_a + \frac{1}{2.303} \ln \frac{b}{a-b}.$$

$$\therefore \frac{\partial(\text{pH})}{\partial b} = \frac{1}{2.303} \cdot \frac{a-b}{b} \left[\frac{a}{(a-b)^2} \right], \text{ or } \frac{\partial b}{\partial(\text{pH})} = 2.303 \frac{b(a-b)}{a}.$$

$$\text{i.e., Buffer capacity, } \beta = 2.303 \frac{b(a-b)}{a}, \text{ or } \frac{d\beta}{db} = \frac{2.303}{a} (a-2b)$$

When $b = a/2$, $d\beta/db = 0$, that is, β is maximum or minimum at half-neutralisation point. But

$$\frac{d^2\beta}{db^2} = -\frac{2.303 \times 2}{a} \text{ which is negative.}$$

Hence, the half-neutralisation point is maximum for β .

ADSORPTION : ELECTROKINETIC POTENTIAL

XIV.1. Adsorption. When a component in a heterogeneous system penetrates into another and spreads throughout the bulk of the latter it is regarded as *absorption*, the first is absorbed by the second. Ammonia gas is absorbed by water when it comes in contact with it. But it is now well-known that often a component (A), instead of penetrating inside another, remains relatively more concentrated near or on the interface *i.e.*, surface of separation. The result is, the concentration of A in the vicinity of the interface is different from that in the bulk. This phenomenon is called *adsorption* and it is necessarily related to the surface.

If a finely divided solid (say, charcoal powder) is stirred into a dilute solution of methylene blue, the depth of colour of the solution decreases appreciably. Similarly if a finely divided solid is added to a gas at low pressure, the gas pressure is found to decrease. In these instances, the dye or the gas concentrates on the surface of the solid and is said to have been adsorbed. A clear-cut distinction between the amounts absorbed and adsorbed is not quite easy and the word *sorption* is sometimes used to include both the physical processes.

The substance on the surface of which adsorption occurs is the *adsorbent* and the substance adsorbed is termed *adsorbate*. The magnitude of adsorption depends upon (i) the nature of the adsorbent and its state of subdivision, (ii) the nature of the adsorbate and its concentration or pressure and (iii) the temperature.

XIV.2. Gibbs Adsorption Equation. Before dealing with the experimental observations on adsorption, it would be worthwhile to discuss it from thermodynamical standpoint. A relation between the amount of adsorption and the surface tension can be easily derived by considering a thermodynamical cycle of the following type.

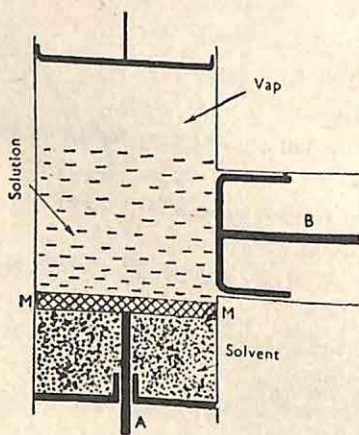


FIG. XIV.1 (MM, semipermeable membrane)

Starting with a dilute solution of volume v , surface area s and osmotic pressure π , we first allow the surface to increase at constant volume, then the volume is increased without any change in surface. Subsequently, the original surface and volume are restored. Suppose the solution is taken in a vessel as in Fig. XIV.1, in which the solution is in contact with a vapour phase consisting only of the vapour of the solvent. The solution is kept separated from a reservoir of solvent through a semipermeable membrane which is fitted with a piston A. The vessel is also fitted with another piston B by which the surface area of solution may be altered. Let γ be the surface-tension of the solution. The

steps are :

1. The surface area is increased, with the help of piston B, by an amount ds , volume remaining constant ; the work done = $-\gamma ds$.

The osmotic pressure may have changed and, if so, its value should be

$$\left[\pi + \frac{\partial \pi}{\partial s} ds \right].$$

2. The volume of the solution is now increased by dv , by pulling out the piston A, the work obtained = $\left(\pi + \frac{\partial \pi}{\partial s} ds \right) dv$. The surface is supposed to remain constant, but due to dilution the surface tension is altered to the value,

$$\left(\gamma + \frac{\partial \gamma}{\partial v} dv \right).$$

3. The surface area is now contracted to its original value, by pushing B back, the work obtained $= \left(\gamma + \frac{\partial \gamma}{\partial v} dv \right) ds$.

The osmotic pressure has now come back to its initial value.

4. Finally, the piston A is pushed back to restore the original volume of the solution, the work done $= -\pi dv$.

The complete cyclic process is carried out isothermally and reversibly so that the net work is nil, i.e.,

$$-\gamma ds + \left(\pi + \frac{\partial \pi}{\partial s} ds \right) dv + \left(\gamma + \frac{\partial \gamma}{\partial v} dv \right) ds - \pi dv = 0.$$

$$\text{or} \quad \frac{\partial \pi}{\partial s} = - \frac{\partial \gamma}{\partial v} \quad \dots \text{(XIV.1)}$$

It is well established that the surface-tension γ changes with concentration of a solution and hence with volume v . Hence equation (XIV.1) predicts that osmotic pressure will also vary with surface area s . But this is possible only if concentration (c) in the bulk of the solution also changes with alteration in surface area, since π is proportional to c . Such a situation would arise only if the concentration in the surface layer is greater or less than that in the bulk of the solution.

Now suppose we take a solution in which n moles of solute are dissolved in volume v . If Γ moles of solute be retained by unit area of the surface, the total quantity of the solute taken up by the surface is Γs .

Then the concentration in the bulk of the solution, $c = \frac{n - \Gamma s}{v}$.

$$\text{So that,} \quad \left(\frac{\partial c}{\partial v} \right)_s = - \frac{(n - \Gamma s)}{v^2} = - \frac{c}{v} \quad \dots \text{(A)}$$

$$\text{and} \quad \left(\frac{\partial c}{\partial s} \right)_v = - \frac{\Gamma}{v} \quad \dots \text{(B)}$$

$$\text{Rewriting equation (XIV.1),} \quad \frac{\partial \pi}{\partial c} \cdot \frac{\partial c}{\partial s} = - \frac{\partial \gamma}{\partial c} \cdot \frac{\partial c}{\partial v}$$

Substituting from (A) and (B), and remembering $\pi = cRT$, we have

$$RT \left(- \frac{\Gamma}{v} \right) = - \left(- \frac{c}{v} \right) \cdot \frac{d\gamma}{dc}$$

$$\left. \begin{array}{l} \text{or} \quad \Gamma = - \frac{c}{RT} \cdot \frac{d\gamma}{dc} \\ \text{i.e.,} \quad \Gamma = - \frac{1}{RT} \cdot \frac{d\gamma}{d \ln c} \end{array} \right\} \quad \dots \text{(XIV.2)}$$

This is known as *Gibbs adsorption equation*.

Since usually $\frac{d\gamma}{dc}$ has a positive or negative value, Γ is not zero. That is, the concentration in the surface layer is different from that in the bulk. When $\frac{d\gamma}{dc}$ is negative, the value of Γ is positive, i.e., there is *positive adsorption*. In solutions for which $\frac{d\gamma}{dc}$ is positive, Γ will be negative, there would occur *negative adsorption*, sometimes called *desorption*.

For most of the solutions, the surface tension decreases with increase in concentration *i.e.*, dy/dc is negative ; hence Γ is positive. It means an excess concentration in the surface layer. Adsorption is thus a thermodynamical necessity.

Attempts to verify the equation was first made by McC Lewis (1908). A stream of drops of oil or mercury was led through a long column of caffeine or dyestuff solution. The number and size of the oil or mercury drops were known, so that total interface-area was known. The initial concentration and also the concentration of the solution after the drops had passed through were estimated. The value of Γ , the amount removed by the surface by adsorption, was thus known. The right-hand side was separately evaluated by measuring dy/dc experimentally. The value of Γ , the amount adsorbed was found to be somewhat higher than that predicted by the equation. Donnan and Barker repeated the experiment with nonylic acid and saponin solutions through which air bubbles of known dimension were passed. Here also the results showed that the amounts adsorbed were somewhat greater than those calculated from the equation. McBain and his co-workers (1927) followed a different technique with solutions of camphor, amyl alcohol, phenol, hydrocinnamic acid etc. The terminals of a narrow trough filled with solution were coated with a hydrocarbon. The solution then bulged out a little above the terminal of the vessel. With a swiftly moving microtome blade the surface layer was cut off and collected in a metal receptacle. Using a sensitive interferometer, the difference in the concentration at the surface and in the bulk was determined. The results agreed well with the requirements of the equation. The equation was thus experimentally directly verified.

XIV.3. Adsorbent and Adsorbate. It is generally believed that gases are adsorbed on the surface of all solids but the effects become noticeable only when the surface area of the adsorbent for a given mass is quite large. For this purpose, therefore, the adsorbent must be sufficiently porous and in a finely divided state. Charcoal, silica gel, platinum black, nickel powder etc. are very effective as adsorbent for they have large exposed surfaces to take up appreciable quantities of different gases. The adsorbents are sometimes specially treated to raise their adsorbing qualities. Charcoal prepared from bone or coconut shells are heated to about 1000°C in vacuum or in chlorine. Such treatment distils away the hydrocarbon impurities from charcoal rendering its surface free and clean where adsorption would readily occur.

A gas is adsorbed in different amounts on different adsorbents. Hydrogen is strongly adsorbed on nickel surface but not so on alumina surface under identical conditions. On the other hand, the amounts of various gases adsorbed on a given surface are different. This implies that the extent of adsorption also depends upon the nature of the adsorbate. This is illustrated in the table here.

TABLE : VOLUMES (x) OF GASES ADSORBED BY 1 GM OF CHARCOAL AT 15°C UNDER 1 ATMOSPHERE

Gas	Volume adsorbed (x c.c.)	B. pt. ($^{\circ}\text{K}$)	Cr. temperature ($^{\circ}\text{K}$)
O_2	8.2	90.2	154
N_2	8.0	77.3	126
H_2	4.7	20.3	33
CH_4	16.2	111.7	190
CO_2	48.0	—	304
HCl	72	188	324
NH_3	181	239.7	406
Cl_2	235	238.5	417

Evidently, there is a parallelism between the extent of adsorption of a gas on a surface and the boiling point or critical temperature of the adsorbate. Easily liquefiable gases, consequently having large cohesive forces, are more readily adsorbed. It should however be realised that it does not mean that in the adsorbed state the adsorbate is in liquid phase.

The amounts of gases adsorbed is either measured gravimetrically from the increase in weight of the adsorbent or volumetrically from the variation in pressure. The diagrammatic sketches of the apparatus used are given in Fig. XIV.2.

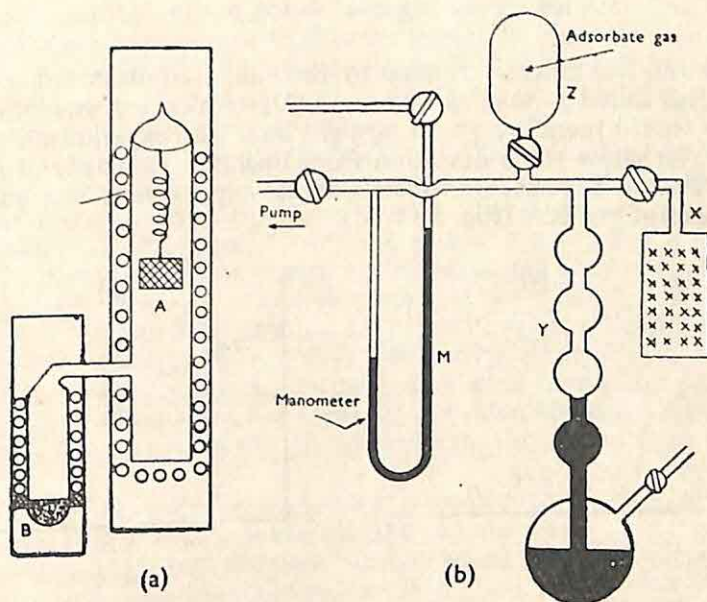


FIG. XIV.2 Apparatus used for the measurement of gas adsorption.
(a) McBain gravimetric balance (b) Volumetric apparatus.

In the McBain gravimetric balance for adsorption [Fig. XIV.2(a)], a known amount of adsorbent taken in a small platinum thimble (A) is suspended from a previously calibrated quartz spiral. The elongation of the spiral read with a travelling microscope gives the weight of the thimble. The glass tube containing the spiral is connected to another tube (B) at the bottom of which is placed a small amount of solid adsorbate (if necessary surrounded by freezing agents). The whole tube is evacuated and finally sealed. The adsorbate tube (B) is then carefully heated electrically to a definite temperature, the vapour pressure being known from the temperature. The spiral-containing tube is also maintained at a desired temperature by carefully heating the same electrically. The amount of gas adsorbed is known from the elongation of the spiral. Measurements may be made at different temperatures.

In Fig. XIV.2(b), the adsorbent is taken in a container X connected to the adsorbate-gas reservoir Z, a calibrated gas burette Y and a manometer M. The volumes of the different parts of the apparatus are previously calibrated. The system is first evacuated and then the gas is admitted. The pressure readings when equilibrium is reached would enable one to calculate the volume of gas adsorbed.

XIV.4. Adsorption Isotherm. The extent of adsorption on a given surface generally increases with increase in pressure. At low temperatures the adsorption of a gas increases very rapidly as the pressure rises. When the temperature is high, the increase in adsorption is relatively less.

The relation between the amount adsorbed by an adsorbent and the pressure (or concentration) of the adsorbate at a constant temperature is called the *adsorption isotherm*. This variation of adsorption with pressure is often represented empirically by the expression,

$$\frac{x}{m} = kp^n \quad \dots \text{(XIV.3)}$$

where x gms of gas are adsorbed by m gms of adsorbent at pressure p , so that x/m denotes the amount of gas adsorbed by unit mass of the adsorbent. n and k

are constants depending upon the nature of adsorbate and adsorbent. n is always greater than unity, which means that the amount of adsorption does not rise as rapidly as the pressure. Taking logarithms of both sides, equation (XIV.3) becomes

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \quad \dots (XIV.4)$$

This relation was extensively used by Freundlich in measurements of adsorption and is often called *Freundlich isotherm*. A graphical representation of $\log x/m$ against $\log p$ would therefore give a straight line. The experimental values, when plotted, however show some deviation from linearity, especially at low temperatures. This relation is hence considered as an approximate one and is suitable for small ranges of pressure (Fig. XIV.3a).

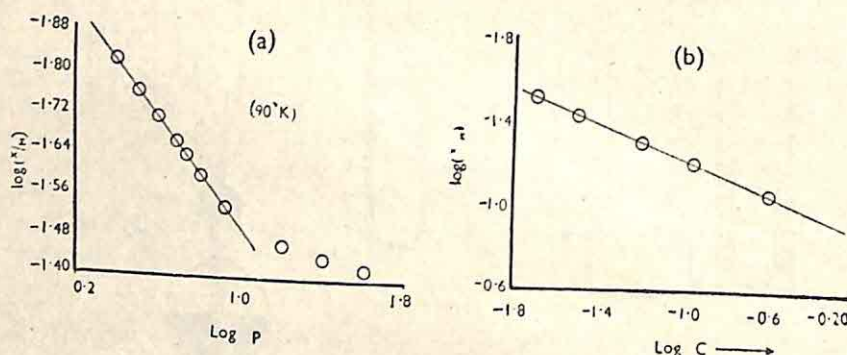


FIG. XIV.3 Adsorption isotherm. (a) N_2 on mica at 90°Abs.
(b) Acetic acid on charcoal at 25°C

This isotherm is also extensively used for adsorption of solutes from solution and has been found satisfactory. The pressure in the expression is replaced by equilibrium concentration (c) of the solute, i.e.,

$$\frac{x}{m} = kc^{\frac{1}{n}} \text{ or } \log x/m = \log k + \frac{1}{n} \log c, \quad \dots (XIV.5)$$

k and n are empirical constants depending on the system and the temperature. The relation can be tested quite easily. A known quantity of blood charcoal may be added to equal volumes of dilute solutions of acetic acid at different concentrations and shaken at a constant temperature. The concentration of the acid at equilibrium is then determined by titration. The values of $1/n$, determined by Freundlich from the slope of the curves $\log x/m$ vs $\log c$, for different acid solutes on charcoal are given below (see Fig. XIV.3b).

TABLE : ADSORPTION OF ACIDS ON BLOOD CHARCOAL

Solute	$\frac{1}{n}$	Solute	$\frac{1}{n}$
Acetic acid	0.425	Succinic acid	0.243
Propionic acid	0.394	Benzoic acid	0.338
Butyric acid	0.301	Picric acid	0.240

Langmuir's Adsorption isotherm. As to the mechanism of the process of adsorption of gases it was, in the beginning, generally accepted that due to physical forces the gas molecules were attracted towards the surface of the solid adsorbent. In the immediate vicinity of the surface the gas remains in a highly dense state and with increasing distance from the surface the gas becomes more rarefied until the density becomes the same as that in the bulk of the gas. The failure of Freundlich isotherm at higher pressures and some other observations however indicated that this concept of physical adsorption might not be entirely correct. In 1916, Langmuir introduced a new concept involving chemical forces. According to him, in the interior of the solid adsorbent, the atoms have their field of force wholly

satisfied by the surrounding atoms. The atom of the adsorbent on the surface are not completely surrounded and these have a residual force due to unshared electrons towards the exterior. This residual field leads to sharing of electrons with striking gas molecules and a sort of covalency-linking is formed between the adsorbate gas molecule and the surface atom. The distinction between this linkage and the formation of a chemical compound is that in spite of the electron sharing with the gas molecule, the surface-atom of the adsorbent remains simultaneously bonded with the other atoms in the crystal-lattice. The adsorption is thus chemical in nature and hence often called chemisorption.

It is further contended that (i) the surface of the adsorbent is a "chequer-board" of atoms upon each of which a gas molecule may be adsorbed. (ii) The residual field of force extends approximately up to a distance equal to that of molecular diameter. Hence, once the surface atoms are covered up by the gas molecules, no further adherence of the gas molecules would occur, i.e., the adsorbed gas is *unimolecular* in thickness. Initially every gas molecule striking the surface gets adsorbed, but thermal agitation has an opposite effect whereby some of the adsorbed molecules would evaporate off. Ultimately an equilibrium is reached when the rate of adsorption equals that of evaporation or desorption. (iii) Since adsorption would involve electron sharing, considerable heat-changes would occur resulting into activation of the adsorbed gas molecules.

Experimental evidence in support of the fact that chemical forces are involved in adsorption and that unimolecular layer is formed was also obtained by Langmuir.

(i) The electron emission from a tungsten filament heated at 1900°K was observed to be considerably reduced when traces of oxygen at pressure 10^{-6} atm was introduced. The tungsten also failed to carry on the dissociation of H_2 into atoms on its surface in this condition nor did the oxygen combine with hydrogen which it normally did at 1500°K . It means that oxygen had covered up the tungsten surface and has formed a stable film. It has not formed the oxide WO_3 , for in that case WO_3 would distil away even at 1000°K . In fact, on prolonged heating tungsten oxide was formed which evaporated off leaving clean solid surface and electron emission was restored. Such a stable nature of the oxygen-film on the tungsten clearly indicated the chemical nature of adsorption.

(ii) On studying the adsorption of N_2 , Argon, CO , CH_4 etc. on smooth surfaces of glass, mica and platinum, Langmuir found that in every case about 0.6×10^{15} molecules were adsorbed per sq. cm. The constancy of this value indicated that layer of same thickness were formed in each case. Assuming interatomic distance on the crystal lattice to be $3\text{\AA}$, the number of surface atoms per sq. cm. is also of the order of 10^{15} . It is therefore reasonable to conclude that unimolecular films are formed on the surface.

(iii) If the unimolecular film theory is accepted, the adsorption of gas would increase with pressure and would ultimately reach a limiting value when the entire surface was covered. This was actually observed in many cases.

Moreover very small amounts of suitable poisons, hardly sufficient to produce a monomolecular film, were able to reduce the adsorptive power of a surface to a negligible amount. In the case of oil films formed on liquid surface, their unimolecular nature was also directly demonstrated by Langmuir (see Sec. XIV.7). All these clearly point to the formation of unimolecular layer of gas, during adsorption, on solid surfaces.

Langmuir also deduced a relation between the amounts of adsorption and the pressure. Let μ be the mass of gas striking per sq. cm of the surface per second of which α fraction gets adsorbed. Suppose θ is the fraction of the surface already covered by adsorbed gas molecules, the bare portion of the surface where fresh adsorption may occur is $(1 - \theta)$. Then,

Rate of adsorption = $\alpha(1 - \theta)\mu$, and rate of desorption = $\beta\theta$ where α and β are constants for a given system.

At eqm. the two rates are equal, i.e., $\alpha(1 - \theta)\mu = \beta\theta$

$$\text{i.e.,} \quad \theta = \frac{\alpha\mu}{\beta + \alpha\mu} \quad \dots (A)$$

Now suppose η gm-moles of gas are adsorbed per unit area. Assuming the

surface to be uniform η is proportional to the quantity adsorbed per gm of the adsorbent, i.e.,

$$\eta = k' \frac{x}{m}$$

The number of molecules adsorbed per sq. cm is ηN_0 where N_0 is Avogadro number. Further suppose there are N_s atoms of adsorbent present per unit area of surface where adsorption could take place. The fraction of surface covered by adsorption (θ) is thus $\frac{\eta N_0}{N_s}$ assuming unimolecular thickness of the adsorbed layer. So

$$\theta = \eta \frac{N_0}{N_s} = k' \frac{x}{m} \cdot \frac{N_0}{N_s} = k'' \frac{x}{m} \quad \dots (B)$$

remembering that N_s is constant for a given system.

From the kinetic theory it is found that μ , the mass of gas striking per unit area is given by

$$\mu = \sqrt{\frac{M}{2\pi RT}} \cdot P = k''' P \quad \dots (C)$$

where P is the pressure of the gas, the temperature is constant. The substitution of μ in equation (A) gives a relation between pressure (P) and the fraction of the surface covered (θ) as

$$\theta = \frac{aP}{1 + aP} \dots (a \text{ is a constant}) \quad \dots (D)$$

On the other hand substituting (B) and (C) in (A) we find

$$k'' \frac{x}{m} = \frac{ak'''P}{\beta + ak'''P}$$

or

$$\frac{x}{m} = \frac{k_1 k_2 P}{1 + k_1 P} \quad \dots (XIV.6)$$

where constant $k_1 = \frac{ak'''}{\beta}$ and $k_2 = \frac{1}{k'''}$, (a , β and k -terms are all constants).

This relation between the pressure and the amount adsorbed at a constant temperature is the *Langmuir adsorption isotherm*. Rewriting,

$$\frac{P}{x/m} = \frac{1}{k_1 k_2} + \frac{P}{k_2} \quad \dots (XIV.7)$$

That is, if $\frac{P}{x/m}$ be plotted graphically against P , a straight line is predicted. This has actually been experimentally realised in many cases of adsorption. In Fig. XIV.4. two such plots of $\frac{P}{x/m}$ vs P for nitrogen and ethylene adsorption are

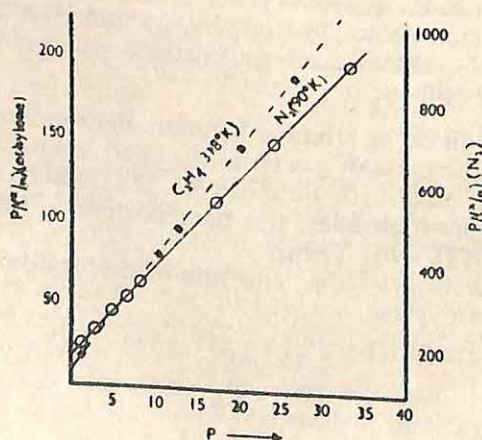


FIG. XIV.4 Langmuir adsorption isotherm

given which establish the correctness of Langmuir's assumption of unimolecular adsorption layer and the isotherm based on the same.

Two limiting cases of the isotherm are particularly interesting. (i) When pressure of the gas is very low or α is very small, k_1P is negligible compared to unity. It means θ , the fraction covered by adsorption, is quite small. In such a case, eqn. (XIV.6) reduces to

$$x/m = k_1 k_2 P \quad \dots \text{(XIV.7)}$$

i.e. adsorption is directly proportional to pressure.

(ii) When the pressure is very large or the surface is almost wholly covered by adsorption, θ is almost equal to unity we have

$$\frac{x}{m} = \frac{k_1 k_2 P}{k_1 P} = k_2 \quad \dots \text{(XIV.8)}$$

i.e. adsorption reaches its limiting value corresponding to a unimolecular layer. At intermediate pressures therefore the amount of adsorption will follow a relation,

$$\frac{x}{m} = kP^{\frac{1}{n}} \text{ when } \frac{1}{n} \text{ lies between 1 and 0.}$$

This indeed is the Freundlich isotherm.

Instances are known where deviations from Langmuir's isotherm are found. This may be due to several causes, e.g. non-uniformity of surfaces, formation of multiple layers in some cases, partial absorption or chemical reaction of the adsorbate with the adsorbent etc.

XIV.5. Types of Adsorption. During the first three decades of this century innumerable investigations were made on adsorption of gases under different circumstances with various systems. A careful analysis of the results of these investigations has led to the inescapable conclusion that there are two different types of adsorption; one is the *chemical adsorption or chemisorption* and the other *physical adsorption or van der Waals adsorption*. The observed characteristics of any adsorption process usually allow it to be placed in one or the other category.

All gases have a tendency to be held to the surface by physical forces and thus exhibit van der Waals adsorption, but when valence forces also come into play in adhering the molecules to the surface, chemisorption ensues. In both types there is a decrease in the extent of adsorption with rise in temperature, hence the processes are exothermic.

In van der Waals adsorption, the heat of adsorption is relatively small, about 5 Kcals/mole which are of the same order as heats of vaporisation. On the other hand in chemisorption, larger amounts of heat of adsorption are involved, about 20 to 100 Kcals/mole, as usually found in chemical reactions. The physical adsorption is more pronounced at temperatures below the boiling point of the adsorbate whereas the chemisorption occurs usually at high temperature. The physical adsorption equilibrium is established rapidly and is generally reversible but in chemisorption the attachment is much stronger, the equilibrium is attained relatively slowly and is irreversible in the sense that if subsequently pressure is reduced, desorption may not occur. In physical adsorption multilayers are formed whereas in chemisorption most commonly a unimolecular layer occurs governed by Langmuir isotherm. The extent of van der Waals adsorption is more a function of the adsorbate than the adsorbent but the amount of adsorption in chemisorption is characteristic of both adsorbate and adsorbent.

Many instances of adsorption are neither one type nor the other, but a combination of the two. A typical isotherm for a chemical adsorption is often found as in Fig. XIV.5(a), the extent of adsorption increases with pressure and ultimately reaches a limiting value. In some instances of simple monolayer physical adsorption attended with small heat-change at low pressures and moderate temperatures, also similar isotherm-curves are found.

But in van der Waals adsorption involving multilayer formation at low temperatures, at least four other types of isotherm-curves are found experimentally. These are shown in Fig. XIV.5.

Such varied types of adsorption was subsequently explained by a theory developed by Brunauer, Emmett and Teller. They extended the Langmuir's concept and proposed that even after the formation of the monolayer, other

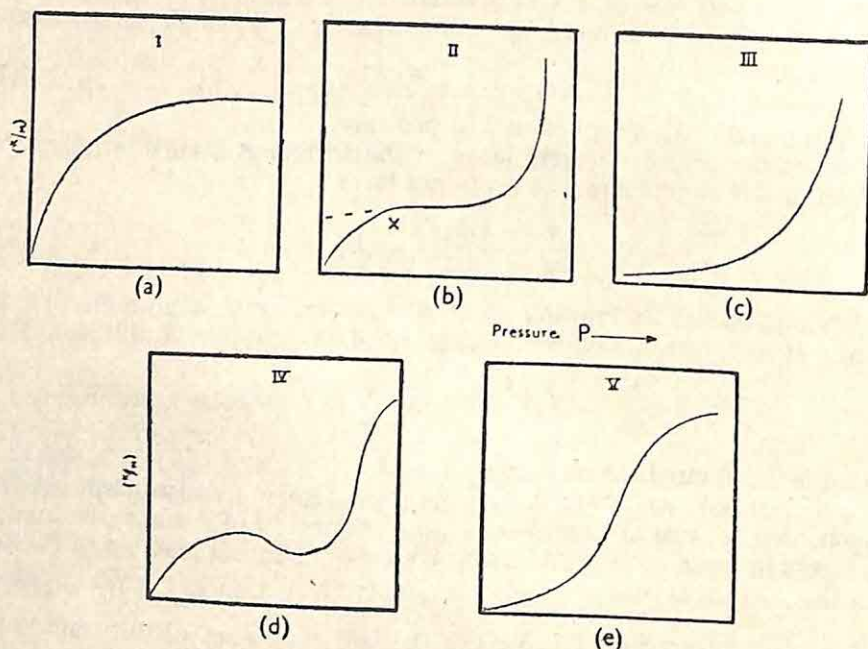


FIG. XIV.5 Adsorption isotherm

layers of the adsorbate gas may condense on it. That is, adsorption is multimolecular, though the Langmuir idea of fixed adsorption sites was retained. There is an equilibrium between the first layer and the adsorbent, and further similar dynamic equilibrium exists for successive molecular layers. The forces that produce condensation are responsible for the binding energy in the successive multimolecular layers. The relation derived on this basis is expressed as

$$\frac{p}{v(p^0 - p)} = \frac{1}{v_m \cdot c} + \left(\frac{c-1}{v_m \cdot c} \right) \frac{p}{p^0} \quad \dots \text{(XIV.9)}$$

This is often called B-E-T equation after the names of the authors where

v = volume of gas adsorbed under pressure p , when p^0 is the saturated vapour pressure at the same temperature.

v_m = volume of gas adsorbed when the surface is covered with a unimolecular layer

and c = a constant for a given adsorbate, such that $c = e^{(E_1 - E_L)/RT}$ in which E_1 is the heat of adsorption in the first layer and E_L heat of liquefaction of the gas.

A simplified derivation of the B-E-T relation is given in appendix-3.

The B-E-T relation suggests that the plot of $\frac{p}{v(p^0 - p)}$ vs $\frac{p}{p^0}$ should be linear.

This has been found to be so experimentally which confirms the correctness of the relation. The intercept $\frac{1}{v_m c}$ and the slope $\frac{c-1}{v_m c}$ from the linear graph enable one

to obtain both v_m and c . It is easy to see, when only unimolecular film is formed on the surface this relation would reduce to the Langmuir isotherm.

Adsorption isotherm of the types II and III (Fig. XIV.5) are explained as that when $E_1 > E_L$ the curve II results but when $E_L > E_1$ the resulting curve is of the type III.

For understanding types IV and V isotherms, it is necessary to assume that not only multilayer adsorption occurs but also that the pores and capillaries of the

adsorbent are filled by condensation at a pressure much lower than the saturation pressure p^0 . Type IV is obtained when $E_1 > E_L$ and type V when $E_L > E_1$.

XIV.6. Surface Area of Adsorbents. Since the adsorbent is used in a fine state of subdivision and is often porous, the determination of its surface area is quite difficult. The B-E-T isotherm is now-a-days extensively employed for such determination of surface areas.

The procedure depends upon finding out the volume of gas (v_m) required to form a unimolecular adsorbed layer. Generally adsorption of nitrogen on the surface is studied, sometimes krypton or *n*-heptane, etc. are also used. We have already seen how v_m is determined from B.E.T. isotherm. In an isotherm of type II (Fig. XIV.5) the point x corresponds to the condition when unimolecular layer is formed. If v_x be the volume of gas at x , reduced to standard temperature and pressure ($P_0 = 1$ atm, $T_0 = 273^\circ K$), then the number of gm-moles of

gas adsorbed is $\frac{P_0 v_x}{RT_0}$. If β be the area occupied by each molecule of nitrogen, then

surface area (S) covered by adsorbed nitrogen is

$$S = \frac{P_0 v_x}{RT_0} \cdot N_0 \beta, \quad (N_0 \text{ being Avogadro number}).$$

The value of β , i.e., area occupied by individual molecule of nitrogen is obtained from its density at its boiling point ($-195^\circ C$).

$$\beta = \left(\frac{M}{d \times N_0} \right)^{\frac{2}{3}}, \quad (d \text{ is the density of liq. nitrogen.})$$

The value of β , from this relation is found to be $16.2 \text{ \AA}^2$. The surface area S is generally expressed in units of square cms per gm.

Langmuir's isotherm may also be used to calculate the surface area, but the results are less satisfactory. There are other methods also in use now. Some of the results are appended below.

TABLE : SURFACE AREAS OF ADSORBENTS DETERMINED FROM B.E.T. ISOTHERM

Adsorbent	Adsorbate used	Area per molecule $\text{\AA}^2$	Vol. adsorbed to produce a mono-layer	Surface area per gm of adsorbent (sq. cm.)
Ni	Kr	14.6	—	9×10^4
Ni	<i>n</i> -butane	24.5	—	8.5×10^4
Cu (fused)	N_2	16.2	0.09	0.39×10^4
Fe- Al_2O_3	N_2	16.2	2.86	12.4×10^4
Silica-gel	N_2	16.2	116.2	500×10^4

XIV.7. Surface Films on Liquids. We may now turn our attention to the adsorption on liquid surfaces. Minute quantities of oil added to water will spread and form thin films on the surface. Other insoluble substances such as long chain fatty acids like stearic acid, oleic acid etc., also spread out on the surface of water. The spreading is to be regarded as a case of adsorption of one liquid on another.

When a long chain fatty acid, say stearic acid, $CH_3(CH_2)_{16}COOH$, comes in contact with water, $-COOH$ group is strongly attracted towards water while the hydrocarbon chain is hydrophobic and prevents it from dissolving. The net result is that it spreads out and generally forms, as we shall see, a unimolecular layer on the water surface. The study of such surface films is nowadays made with a Langmuir film balance as in Fig. (XIV.6).

A shallow tray is filled to the brim with water. A light mica float just less than the width of the trough is placed on water at a fixed position near one end. At the extremities of the float two thin Pt-strips are attached to prevent any leakage of an oil film on the surface. The float is rigidly attached through an unspun silk fibre to a delicate torsion wire balance placed vertically above it. It is thus possible to measure any lateral pressure on the float from the torsion balance.

Near the other end of the trough is a movable compressing barrier of thin glass plate placed parallel to the float. The barrier is mounted on a screw moving along a scale, so that the area between the float and the barrier is easily known. From a microsyringe a drop of a benzene solution of stearic acid of known

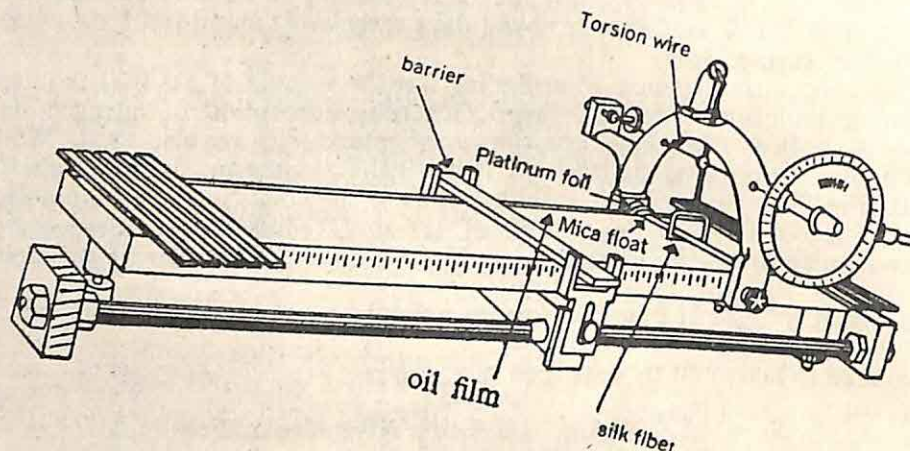


FIG. XIV.6 Langmuir film balance

concentration is added to the surface of water. The benzene evaporates off and an oily film spreads on the surface of water between the float and the barrier. The quantity and hence the number of molecules of stearic acid on the surface is known. So long the area is relatively large, the molecules in the oily film move about freely as is evident from the motion of the lycopodium dust added on the film surface. The barrier is then pushed slowly towards the float, *i.e.*, the area of the oil film is reduced. In such compression of the film, initially no change in the lateral pressure on the float is noticed from the torsion balance. But soon a critical limit of compression of the area is reached. Suddenly at a point the film becomes rigid, the dust particles do not move and fine strain lines begin to appear on the film. At this point, any attempt to reduce the film area even slightly is found to register in the balance a sudden steep-rise in the lateral pressure on the float. Further contraction of the area crumples up the film altogether. If the pressure on the float is plotted against the surface area per molecule, a curve of the type shown in Fig. XIV.7 is obtained. At the point *b*, the film becomes rigid and the lateral pressure rises steeply to the point *c*, after which the film buckles and folds on further reduction of area. When this critical point is reached, the area per molecule is found to be $20.5 \text{ \AA}^2$. It is most significant, the same critical limit of area (about $21 \text{ \AA}^2$) is obtained when other long-chain fatty acids, like palmitic or oleic acid, are used in place of stearic acid.

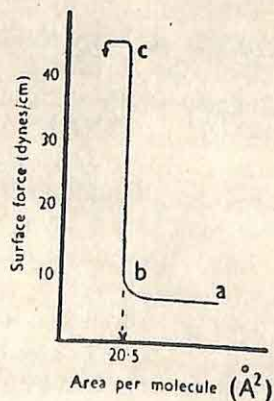


FIG. XIV.7 Pressure-area isotherm for surface film on liquids

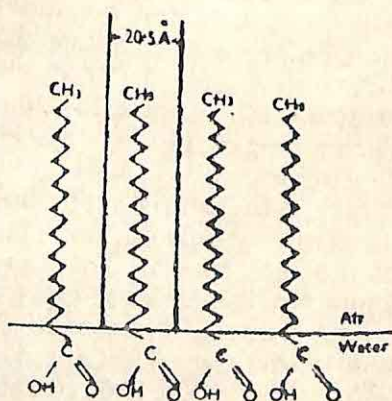


FIG. XIV.8 A monomolecular oriented surface film on water

From these observations, it is justifiably reasoned that initially the surface was not completely covered by the film and the molecules could freely move about on the surface. On compression of the area when the point *b* is reached the molecules are most close-packed, the entire area is just covered by the film molecules forming a monomolecular layer; any attempt to compress it further is opposed by the film. That the same result is obtained with different acids show further that the molecules in the film must be similarly oriented having their $-\text{COOH}$ groups in water and hydrocarbon residues away from water. The physical picture would be somewhat like that shown in Fig. XIV.8.

An approximate calculation of the cross-section of a stearic acid molecule may be made in the following way.

The length of the zig-zag chain of stearic acid molecule $= 17 \times 1.25 = 21.25 \text{ \AA}$

$$\text{The volume of the molecule} = \frac{M}{\rho} \cdot \frac{1}{N_0} = \frac{284}{0.85} \times \frac{1}{6 \times 10^{23}} = 550 \text{ \AA}^3$$

$$\text{Hence the cross-section of the molecule} = 550/21.25 = 25.8 \text{ \AA}^2$$

This estimate is in fair agreement with the experimental value from Langmuir film experiments. Thus, Langmuir experiments provide an incredibly simple method of obtaining molecular cross-section. Moreover, these results are found to be quite close to the accurate measurements from X-ray diffraction. The microphotographs from the infra-red spectroscopy also support the formation of monomolecular thickness of the film.

The minimum area ($21 \text{ \AA}^2$) occupied by a molecule has been found to be independent of the length of the hydrocarbon chain when any of the following polar groups are present at the terminus of the molecule: $-\text{COOH}$, $-\text{CONH}_2$, $-\text{COCH}_3$, $-\text{COOR}$, $-\text{OH}$, etc. On the other hand if a triglyceride be taken, the value is observed to be about $63 \text{ \AA}^2$ as is expected from its containing three polar groups (Adam).

These simple but convincing experiments by Langmuir and, later on, by Adam and others established (i) the surface films are unimolecular in thickness and (ii) the molecules in the film are oriented. These features of liquid films were, later on, found to be present in gaseous adsorption on solids as well. [See also XV.27].

Similar monomolecular films are also expected on the liquid-liquid interface. If stearic acid is added to an oil-water emulsion, the acid molecules would produce a monomolecular film at the oil-water interface as in air-water interface. In dealing with function of detergents or soaps or with lubricants, such studies are of immense importance.

XIV.8. Applications of Adsorption. Innumerable industrial processes, starting from the synthesis of ammonia to the manufacture of alcohol or synthetic petrol, are heterogeneously catalysed reactions. Most of these catalysed reactions are effected through adsorption of reactants on solid surfaces. Adsorption thus plays a very important as well as an extensive role in industry. We shall discuss this aspect of heterogeneous catalysis in the next chapter.

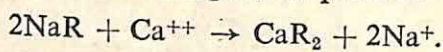
The stabilisation of colloids through adsorption of ions on the particles is of considerable interest both from the practical and the theoretical stand point.

The function of gas masks is based on the preferential adsorption of harmful gases present in the atmosphere by the use of suitable adsorbents in order to purify the air for inhalation. The role of charcoal in the recovery of iodine and of many dyes from their dilute solutions, or its role in the clarification of syrups in sugar industry, etc. are based on its adsorption capacity.

The *chromatographic methods* used widely nowadays in separating and analysing valuable and minute quantities of components from a mixture are also based on adsorption. A suitable adsorbent, often very finely powdered aluminium oxide, magnesium oxide or charcoal, etc., is taken in a long column. The solution containing the components is poured down the column. As the solution trickles down, the solute which is more readily adsorbed is retained in the upper layers of the column together with lesser amounts of the other components. Further

down in the column, the less easily adsorbed component would be adsorbed. Thus, a partial separation of the components is effected in the adsorbent column. Subsequently, small amounts of pure solvent are allowed to run down the column very slowly. The less easily adsorbed solutes will be first removed by this solvent from the upper strata. As this runs down further, the latter would be re-adsorbed in a lower strata. As such distinct layers containing different adsorbed solutes will be formed in the column. The entire column may be taken out and different layers may be cut off separately from which the solutes may be extracted or eluted by using sufficient solvent. This, in brief, is the principle involved in chromatography. When the solutes are coloured the separate layers are easily seen and detected. But if the solutes are not coloured the different layers are detected with exposure of the column in ultraviolet light. In 1931, Kuhn first successfully employed it in separating the carotenes. The successful separation of rare earth elements by chromatographic method using fractional adsorption on organic resins is another outstanding illustration.

Another application of adsorption is found in the use of ion exchangers. It is known for a long time that a soil column would exchange its calcium with potassium when a solution of potassium chloride was led through it. Similar property is also seen in many minerals, such as zeolites, which have the capacity to exchange some of the cations they contain for others in solution. In the softening of water, such properties have been taken advantage of by using zeolites. Synthetic ion exchange resins, Dowex or Amberlites, are now used for ion exchange purposes. The resin is so prepared during polymerisation that it may have either a cation exchange or an anion exchange capacity. A cation-exchange resin would contain a large insoluble polyvalent anion R , to which are attached a number of exchangeable hydrogen ions (H_xR). When this resin is placed in a salt solution ($NaCl$) the sodium resin NaR is formed. This sodium-form when placed in contact with solution having Ca^{++} ions, exchange takes place as



Thus, the calcium present in solution is removed in the insoluble form by adsorption and exchange. When the resin has become saturated with Ca^{++} , a concentrated solution of $NaCl$ is run through and the process is reversed, reproducing the sodium-resin. The capacity of a resin to adsorb different ions is dependent on the charge carried by the ions and their size in hydrated form.

ELECTROKINETIC PHENOMENA

XIV.9. In the early and the middle parts of the nineteenth century, some crude experiments carried out by a number of investigators revealed a set of phenomena which overlapped the domains of adsorption chemistry, colloid chemistry and electrochemistry. These, in later years, came to be known as electrokinetic phenomena. Broadly defined, they represent phenomena involving the relative motion of one phase with respect to another with the exhibition, in certain cases, of some electrical properties. An orderly description of the qualitative aspects of the phenomena followed by the quantitative theoretical formulation will be more useful than a presentation with a heed to the historical sequence of development. There are the following four types of electrokinetic phenomena.

1. *Electro-osmosis* : Suppose some solid powder be made compact in the form of a diaphragm and the latter placed in a liquid which is, at least, poorly conducting. If the diaphragm is fixed in position (Fig. XIV.9), an application of an electrical potential difference across the former results in a motion of the liquid from one side of the diaphragm to the other, i.e., a relative motion of the liquid phase with respect to the solid phase results. This is known as electro-osmosis or electro-endosmosis or simply endosmosis.

The flow of solvent across the diaphragm will result in the rise of the level of liquid in one limb and the consequent increased hydrostatic pressure in the limb would tend to offset the endosmotic flow. A steady state situation will ultimately

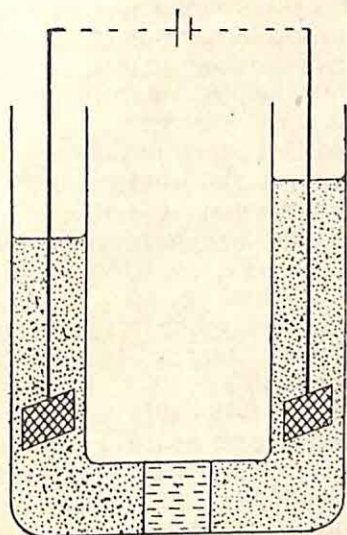


FIG. XIV.9

mately prevail when the effect of endosmotic flow will be neutralised by an equal amount of hydrostatic counterflow.

The fine pores of a diaphragm, necessary for electroosmosis, are after all an agglomeration of numerous randomly arranged capillaries. In essence, therefore, an electroosmotic phenomenon should be observable whenever one subjects a dilute solution containing a fixed capillary or a number of fixed capillaries in it to an external potential field.

Experimentally, the following significant observations, amongst many, have been made from endosmotic experiments.

1. Under comparable conditions, fine particles with greater adsorptive power, such as colloidal grains or coagulum of colloids, making up the diaphragm cause greater endosmotic flow than when the diaphragm is made up of well developed crystalline particles.

2. For a given diaphragm, the greater the conductivity of the solution due to the presence of the electrolyte ions, the less is the endosmotic flow.

II. Streaming potential : In electroosmosis, it is seen that there results a mechanical flow of liquid across a diaphragm or a capillary from an application of an electrical potential. The reverse of this process, called streaming potential, involves a generation of a potential difference between the liquids on either side of a diaphragm or a capillary, when a solvent is forced to flow through the latter by hydrostatic pressure.

III. Electrophoresis : The third type of electrokinetic phenomenon is electrophoresis, also commonly called cataphoresis. Fine grains of solid or liquid or gas held in suspension in a solvent, such as, colloidal particles of clay, emulsion globules or foams, move towards electrodes when an external field is applied. Electrophoresis, thus, constitutes a relative motion of one phase past another phase (viz. dispersion medium) and is, like electroosmosis, a mechanical effect at the expense of an externally applied electrical field.

IV. Sedimentation Potential : The last of these phenomena, and incidentally, also the last one to be discovered, is the sedimentation potential first studied by Dorn. It stands in the same relationship to electrophoresis as does streaming potential to endosmosis. If small grains of an insoluble solid, such as clay particles, are allowed to fall in sufficient number through a long vertical column of dilute solution, an electrical potential difference can be registered between any two points, not in the same horizontal plane, of this column of solution. The points chosen should preferably be far from each other and sufficient number of particles should stream down the solution to cause an effect appreciably enough for experimental discernment.

Electrical double layer : Before a quantitative interpretation of these phenomena can be taken up, it is necessary to understand qualitatively why these processes occur at all.

Whenever one insoluble phase is in contact with another liquid phase—say an aqueous phase—in which there may be present or not electrolyte ions other than its own hydrogen and hydroxyl, an ionic distribution occurs at the interface of the two phases. To be specific, if we consider particles of AgI suspended in water containing a small amount of potassium iodide in solution, iodide ions will be adsorbed to a certain extent on to the surface of each silver iodide particle. This will render the surface negatively charged which would naturally drag some K^+ ions or H^+ ions in its vicinity. At equilibrium, therefore, one can imagine the existence of a double layer at the particle liquid interface. One part of the double layer consists of a negative layer on the surface of each silver iodide particle and the second part of the double layer in the aqueous phase comprises ions with an

overall positive charge predominance. In the case of a simple glass rod dipping in water, possibly the preferential adsorption by the glass surface of H or OH ions of the aqueous medium gives rise to the formation of the double layer.

In certain instances again, insoluble solids or macromolecular particles in colloidal solutions may be ionogenic in character and may form double layer at the interface through self dissociation. This is believed to happen in the case of protein suspensions and sometimes also in clay suspensions. So, whatever be the manner in which a double layer may originate, one can presume its existence at the junction of two phases, one of which at least is a liquid.* Electrical double layer necessarily implies a separation of charges and hence every electrical double layer is the seat of a potential difference.

Different ideas regarding the structure of the double layer at an interface have been put forward. Helmholtz, to whom the original concept of the double layer is due, Gouy and Stern, all held separate views as to its structure. The idea of Stern, mostly accepted nowadays, is briefly described here with qualitative representations in Fig. XIV.10. According to him, in the case of a solid liquid interface, the charges in the first part of the double layer remain fixed on the solid surface at l_1 ; the solution side of the double layer containing the counter ions can be divided into two parts—a fixed part (l_2) of the counter ions at a distance of a few angstroms from the solid surface and another diffuse portion of counter ions with concentration gradually falling off (Fig. XIV.10a) or rising (Fig. XIV.10b) to that uniform value as prevalent in the bulk, say at l_3 .

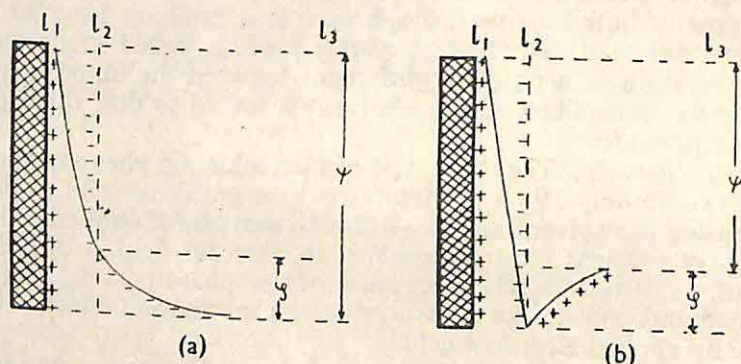


FIG. XIV.10

The ions in the diffuse layer have a limited freedom of movement as compared to that of ions of like charge in the bulk of solution. Under a more or less moderate drastic external condition viz., the impression of an electrical potential difference or the mechanical application of hydrostatic pressure, the ions in the diffuse part of the double layer are swept away tangentially along with the solvent molecules in the region may be surface.

In the undisturbed conditions, there exists a sharp drop of potential from the solid surface (l_1) to the fixed part (l_2) of the double layer on the solution side. It is then followed by a gradual change in potential across the diffuse part upto the bulk of the solution (Figs. XIV.10). The total potential drop from the solid surface (l_1) to the bulk of the solution is called the double layer potential ψ , while the difference in potential between the fixed part of the double layer (l_2) and the solution bulk (i.e., the potential change across the diffuse portion of the double layer) is termed *zeta potential* or *electrokinetic potential* and conventionally represented by the symbol ζ .

XIV.10. Qualitative Interpretation of Electrokinetic Phenomena. The foregoing discussion on electrical double layer helps one to understand the four electrokinetic

*Solid-solid, solid-gas, liquid-gas interfaces are not considered here.

phenomena, which are the different manifestations of the same underlying principle. We shall consider here the case of electroosmosis which would be adequate for our understanding of the remaining three phenomena.

The application of an external d.c. voltage across the two ends of a capillary, with a solution filling it up, will cause the ions in the diffuse part of the double layer to move towards the respective electrodes. The ions in the bulk of the solution will also participate in the migration process. The capillary, being narrow, these ions, especially the ones in the diffuse part, mechanically drag along solvent molecules resulting in a net transfer. A thin layer of liquid sticks fast to the solid surface. On one side of this layer are the charges resting on the solid surface and on the other, are the oppositely charged ions of the fixed part of the double layer. With the electric field on, these latter ions do not respond, but ions in the diffuse part do. Hence electrokinetic movement involves a tangential slipping of a column of liquid against a thin adhering layer.

There is one important distinction between the nature of liquid flow through a capillary under hydrostatic pressure difference (a poiseuille flow) and that under electric potential difference (an endosmotic flow). In the first case, the velocity profile has a parabolic shape and in the latter it is nearly a rectangular one. (Fig. XIV.11 *a* and *b*).

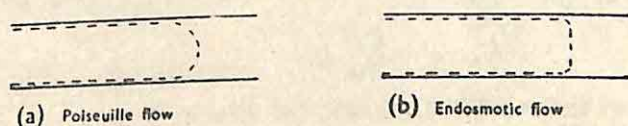


FIG. XIV.11

XIV.11. Quantitative Formulation for Electroosmotic Process. Consider a very thin rectangular cell, having the floor and ceiling areas each equal to 1 sq. cm. Let this cell, which is of very small height and of cross section a , be filled with a solution.

A uniform electric field E , applied parallel to the floor and ceiling, causes an endosmotic flow of the liquid leaving to solid surface with its adhering stationary liquid layer intact. Now, any portion of the moving liquid is subjected to two forces — a driving electric force and a retarding viscous force. Imagine a thin rectangular volume of liquid of 1 sq. cm surface area and height dx at a distance x from the stationary layer moving with a velocity V (relative to the solid surface) under steady state condition. The net retarding drag on this volume element is equal to the difference of the viscous forces on its upper and lower surfaces and is given by

$$\begin{aligned} & \left(\eta \frac{\partial V}{\partial x} \right)_{x=x} - \left(\eta \frac{\partial V}{\partial x} \right)_{x=x+dx} \\ &= \left(\eta \frac{\partial V}{\partial x} \right)_{x=x} - \left[\left(\eta \frac{\partial V}{\partial x} \right)_{x=x} + \frac{\partial}{\partial x} \left(\eta \frac{\partial V}{\partial x} \right) dx \right] \\ &= - \eta \frac{\partial^2 V}{\partial x^2} dx \quad \dots (1) \end{aligned}$$

The electric driving force on this volume element of liquid at a distance x from the stationary layer is $E\rho_x dx$, where ρ_x is the volume charge density at that distance x .

$$\text{For the steady-state, } E\rho_x dx = - \eta \frac{\partial^2 V}{\partial x^2} dx \quad \dots (2)$$

Applying Poisson's equation to connect volume charge density (ρ_x) with the potential (ψ_x) at a distance x due to the combined entity of the solid surface and the stationary liquid film with their charge contents, one obtains

$$\frac{\partial^2 \psi_x}{\partial x^2} = - \frac{4\pi\rho_x}{D}, \text{ or, } \rho_x = - \frac{D}{4\pi} \frac{\partial^2 \psi_x}{\partial x^2} \quad \dots (3)$$

where D is the dielectric constant of the medium. Only x direction is considered, since ψ_x varies with the distance from the stationary film. This ψ_x has no connection with the applied field E , which is entirely arbitrary. Substitution of (3) in (2) yields,

$$\eta \frac{\partial^2 V}{\partial x^2} = \frac{DE}{4\pi} \cdot \frac{\partial^2 \psi_x}{\partial x^2} \quad \dots (4)$$

Integrating, $\eta \frac{\partial V}{\partial x} = \frac{DE}{4\pi} \cdot \frac{d\psi_x}{dx} + C_1 \quad \dots (5)$

As $x \rightarrow \infty$, $\left(\frac{\partial V}{\partial x}\right)_{x \rightarrow \infty} = 0$ and also $\left(\frac{\partial \psi_x}{\partial x}\right)_{x \rightarrow \infty} = 0$

hence, $C_1 = 0$

$\therefore \eta \frac{\partial V}{\partial x} = \frac{DE}{4\pi} \cdot \frac{\partial \psi_x}{\partial x} \quad \dots (6)$

After multiplying by dx and integrating once again, we have

$$\eta V = \frac{DE}{4\pi} \psi_x + C_2 \quad \dots (7)$$

At the stationary layer (i.e., the fixed part of the double layer) where $x = 0$, $V = 0$ and $\psi_x = \zeta$

$\therefore C_2 = -\frac{DE}{4\pi} \zeta \quad \dots (8)$

Again at $x =$ the middle of the cell, the velocity $V = V_m$ and $\psi_x = 0$. Hence from (7), $C_2 = \eta V_m \quad \dots (9)$

Equating (8) and (9), one obtains, $-V_m = \frac{DE}{4\pi\eta} \zeta \quad \dots (10)$

Since V_m represents velocity of the liquid relative to that of the solid ceiling or floor, the minus sign preceding V_m is immaterial, so that one can rewrite (10) as

$$\zeta = \frac{4\pi\eta V_m}{DE} \quad \dots (XIV.10)$$

This relation was first derived by von Smoluchowski and is known as Smoluchowski's equation.

In an experimental set up for the measurement of electroosmotic flow, it is always the volume v of liquid flowing out per second through the capillary or a system of capillaries that is measured. Consequently V_m of the equation (XIV.10) is expressed in terms of v . As has been stated in the previous section, since in endosmotic flow the velocity profile is almost rectangular in shape,

$$v = aV_m$$

Hence

$$\zeta = \frac{4\pi\eta v}{DEa} \quad \dots (XIV.11)$$

The applied electric potential gradient inside the cell can be expressed as

$$E = i \times R = i \times \rho \frac{1}{a} = \frac{i}{ka},$$

where R , ρ and k are respectively the resistance, sp. resistance and sp. conductance of the solution inside the cell and i is the current in amperes. Utilising this relation for E in (XIV.11) and taking proper care of units to express ζ in volts, one gets

$$\zeta \text{ (volts)} = \frac{4\pi\eta k v}{Di} \times (300)^2 \quad \dots (XIV.12)$$

[1 e.s.u. of potential difference = 300 volts.]

Usually the magnitude of ζ , zeta potential ranges between 1 and 50 millivolts. The ζ -potential is greatly altered when salts i.e., ions are added to the solution. The extent of this effect depends both on the concentration and the valency of the ions attracted.

As in endosmosis, Smoluchowski's equation (XIV.10) can be recast in forms suitable for electrophoresis, streaming potential and sedimentation potential experiments. For example, the streaming potential S , under a driving pressure P , is related to the zeta potential by the relation,

$$S = \zeta PD / 4\pi\eta k \quad \dots \text{(XIV.13)}$$

Reference for further reading

1. The physics and chemistry of surfaces—Adam
2. The physical chemistry of surfaces—Adamson
3. The physical chemistry of surface films—Harkins
4. Kinetics of chemical change—Hinshelwood
5. Adsorption of gases by solids—Gregg

Problems

1. The following data were recorded in an experiment on the adsorption of acetic acid from aqueous solution by charcoal :

Conc. of solution (c)	3.6×10^{-3}	8.4×10^{-3}	20.0×10^{-3}	35.0×10^{-3} gm/c.c.
adsorption (x/m)	0.018	0.022	0.028	0.032

Show that the results conform to Freundlich isotherm.

2. In an adsorption of a gas on charcoal the following results were obtained :

P (dynes/cm ²)	3.0	4.0	6.0	9.5	17.0
mass of gas adsorbed (mg/cm ²) $\times 10^3$	14.2	17.6	22.0	28.0	33.0

Examine graphically to what extent Langmuir's equation is applicable.

3. At 0°C, nitrogen was adsorbed on charcoal at different pressures p . The amount of gas adsorbed is expressed in c.c. at N.T.P.

p (mm)	3.90	13.0	23.0	34.0	56.5
b (c.c./gm)	0.99	3.00	5.05	7.00	10.4

Plot the data according to Langmuir isotherm and find out the value of constants of eqn. (XIV.6).

4. Aluminium hydroxide precipitated from a solution containing magnesium sulphate was found on analysis to contain 1% MgO. The ppt. was dissolved again and reprecipitated and then it contained only 0.01% MgO. How do you explain this?

5. An aqueous solution of iodine is shaken with (a) CS₂ and also with (b) charcoal. In each case some iodine was extracted. What are the differences between the two phenomena?

6. 77.1×10^{-6} gms of the alcohol C₁₆H₃₃OH produced a compact film of monolayer on a Langmuir film balance occupying an area of 402.7 sq. cms. Find out the cross section of the molecule.

7. What are the principal features of Langmuir and Freundlich isotherms?

The adsorption of a substance from aqueous solution on charcoal was governed by the relation $\frac{x}{m} = 0.5 C^{0.33}$ in which unit for x/m is gms per gm and concentration is expressed in gms/litre. Find out the quantity of the substance that will be adsorbed by a gm of charcoal from a litre of 0.2% solution.

8. The adsorption of a dye from solution on charcoal is governed by the Freundlich isotherm, in which $n = 2$ and $k = 6.8$. The conc. of the dye is expressed in millimoles/c.c. and the amount adsorbed in millimoles/gm. If 10 gms of charcoal be shaken with a 0.1 M solution of the dye, what will be the eqm. concentration of the solution?

(Ans. 0.0155 M)

CHEMICAL KINETICS : CATALYSIS

XV.1. Introduction. Chemical kinetics is the branch of physical chemistry which deals with a study of the speed of chemical reactions. Such studies also enable us to understand the mechanism by which the reactions occur. In chemical equilibria, only the initial and final states were considered, the energy relations between the reactants and the products being governed by thermodynamics where the time or the intermediate states were of no concern. In chemical kinetics the rate of the reaction process is followed ; in other words, the time variable is introduced. This, we shall see, reveals not only the influence of different factors on the progress of the reaction but it also throws light on the mechanism through which reactant molecules are transformed into products.

There are many reactions for which the kinetic study is not possible. The explosion reactions and most of the ionic reactions occur instantaneously and the velocities cannot be measured. On the other hand, there are reactions which are so slow that months and years are required for any appreciable amount of transformation. In between the very fast and very slow reactions, there are reactions for which the rate can be measured easily : the gaseous reactions like decomposition of HI or N_2O_5 , the reaction in the liquid phase like hydrolysis of ester, mutarotation of glucose etc, come under this category.

It is a common knowledge that apart from the chemical nature, the rates of reaction depend on the concentration of reactants and the temperature. It will be seen later that many reaction rates are greatly influenced by the presence of foreign substances i.e., the catalysts. Also some reaction rates are accelerated by absorption of specific light waves, which are called photochemical reactions. The catalysed and photochemical reactions will be dealt with in later sections.

From the kinetic standpoint, the reactions are classified into two groups ; (a) homogeneous reactions which occur entirely within one phase and (b) heterogeneous reactions where the transformation takes place on the surface of a catalyst or the walls of a container. In the beginning we shall restrict our discussion only to homogeneous reaction kinetics.

Experimental measurement of Reaction Rates. The velocity of a reaction is invariably studied at a constant temperature by maintaining the reaction mixture in a thermostat. The decrease in concentration of the reactants or the increase in the concentration of the products is followed at different time intervals. Both chemical and physical methods of analysis according to suitability are employed in measuring the change in concentration. In chemical methods, definite volume of samples are separated or pipetted out from the reaction mixture and are immediately chilled or diluted with inert media so as to "freeze" the reaction. The freezing of the reaction means abruptly slowing down the reaction or practically stopping the reaction. The samples are then quickly estimated, very often by titration, with suitable reagents. Use of physical methods is often taken recourse to as these are more convenient and accurate than withdrawal and subsequent analysis of samples. The physical measurement is made with the reaction mixture as such and the concentration of a reactant or a product is deduced therefrom. Any physical property of a constituent of the system which changes with the progress of reaction may be taken advantage of. Very frequently optical rotation, refractive index, conductivity, dielectric constant, absorption etc. are measured to pursue the variation in concentration with time. In gaseous reactions which are associated with volume change, dilatometric method is employed or the pressure changes at constant volume may be followed at different time intervals. Special techniques have also been developed to follow the progress of fairly rapid reactions ; for example, in the flow-method two reactants come together through a T-arrangement and as the mixture flows through the tube at a known rate, the conductivity or

absorption of radiation is measured at definite positions along the stream. The extent of reaction at intervals of 0.01 second can be recorded in this way.

Rate of a Reaction. The rate of a reaction, *i.e.*, the velocity of a reaction is the amount of chemical change occurring per unit time. The rate is generally expressed as the decrease in concentration of a reactant or as the increase in concentration of a product per unit time. So, if '*c*' is the concentration of a chosen reactant at any

time *t*, the rate is $-\frac{dc}{dt}$. Or, if the concentration of a product be *x* at any time *t*,

the rate would be $\frac{dx}{dt}$. The reactant or the product chosen should be specified.

The time is usually expressed in seconds. The rate will have units of concentration divided by time. The concentrations are taken in gm-moles/litre, hence rate is moles per litre per second.

XV.2. Order of a Reaction. By stating the order of a reaction, the quantitative dependence of its rate on the concentrations of reacting substance can be indicated. The order is the number of concentration terms on which reaction rate depends. Thus, if the rate of a reaction depends on the first power of the concentration of reactant, *i.e.*,

$$\text{Rate} = kC,$$

then the reaction is said to be of the *first order*. When the rate is proportional to the product of two reactant concentrations or the square of the concentration of a reactant, the reaction is of the *second order*. For example, the decomposition of HI is given by,

$$\text{Rate} = kC_{\text{HI}}^2$$

and the hydrogen-iodine reaction is given by

$$\text{Rate} = kC_{\text{H}_2}C_{\text{I}_2}$$

Both are second order reactions. Hence, if the reaction rate is *experimentally found* to be represented by

$$-\frac{dc}{dt} = kC^n \quad \dots \text{(XV.1)}$$

the order of the reaction is *n*. Generally speaking, if several reactants *A*, *B*, *C* etc. are involved and it is *observed experimentally* that the rate of the process is given by

$$-\frac{dc}{dt} = kC_A^a C_B^b C_C^c \dots \quad \dots \text{(XV.2)}$$

then the order of the reaction would be $n = a + b + c + \dots$. The reaction is said to be of the *a*-th order with respect to *A*, the *b*-th order with respect to *B*, etc.

The order of a reaction may thus be defined as the sum of the exponents of the concentration terms in the rate equation.

Though theoretically reactions of high order are possible, but it is doubtful if reactions higher than third order exist. But there are reactions in which the order is *fractional*, *i.e.*, $n = \frac{1}{2}, \frac{3}{2}$, etc. For instance, the ortho-para hydrogen conversion

has its rate expressed by $\frac{-d[\text{H}_2]}{dt} = kC_{\text{H}_2}^{3/2}$. Similarly the rate of dissociation

of acetaldehyde in gas phase is found to be governed by the relation, $\frac{-d[\text{CH}_3\text{CHO}]}{dt}$

$= kC_{\text{CH}_3\text{CHO}}^{3/2}$. Both the reactions have the order $n = \frac{3}{2}$.

In some heterogeneous or surface reactions, the rate has been found to be independent of concentration. These are *zero-order reactions*. It is important to realise that the order of a reaction and the rate equations are derived from experimental results. Any attempt or theory proposed to explain the mechanism of a chemical process must satisfy the rate equations experimentally observed.

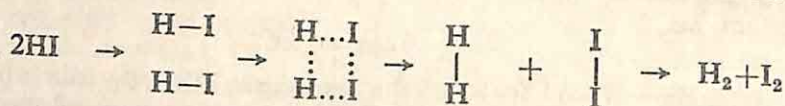
It is also seen that there is no necessary connection between the kinetic order and the form of the stoichiometric equation of a reaction.

For the reaction, $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, the order is one. Again, for the reaction $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$, the order is three halves ($3/2$).

XV.3. Molecularity of a Reaction. The molecularity of a reaction is defined as the number of molecules or atoms which take part in the process of a chemical change. The reactions are said to be *unimolecular*, *bimolecular* or *termolecular* according as one, two or three molecules are involved in the act leading to a chemical change.

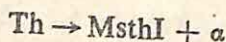
In the early days, no distinction was made between the order and the molecularity of a reaction. The term 'unimolecular' was used for all 1st order reactions, the term 'bimolecular' for 2nd order etc. But the term molecularity, as distinct from the order, of a reaction is now applied in explaining the mechanism of the process.

In the decomposition of hydrogen-iodide, it is believed that when two molecules having sufficient energy come together or collide, the bonds between hydrogen and iodine snap and new bonds between H-atoms and I-atoms are formed, leading to the dissociation. Since two molecules are involved, it is a bimolecular reaction.



Incidentally, the dissociation of hydrogen-iodide is also a second order reaction. In fact all bimolecular reactions are of the second order but all second order reactions are not necessarily bimolecular.

Again, the disintegration of thorium atom as

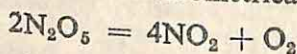


takes place singly and independently. It is thus a unimolecular reaction. This is also a 1st order reaction.

For relatively simple reactions or isolated reactions in which the reactants are directly transformed into product without any intermediate step, the molecularity can be easily defined. But it is now generally known that most of the reactions do occur in a sequence of steps, each step is called an *elementary process*. Every step or elementary process has its molecularity. As such it is not desirable to express molecularity for the overall reaction, as one elementary process may involve two molecules and another step only one molecule.

The molecularity must be integral but the order may be fractional also. Whereas the order of a reaction is obtained from the experimental results, the molecularity is given on the basis of some proposed theoretical mechanism so as to satisfy the experimental findings.

There is also no correlation between the order and the molecularity of a reaction or between the stoichiometric representation and the molecularity. Thus the decomposition of nitrogen pentoxide stoichiometrically represented as



has been found to be of the first order and is believed to have the mechanism as suggested by Ogg (1947) :

- (i) $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$
- (ii) $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{NO}$
- (iii) $\text{NO} + \text{N}_2\text{O}_5 \rightarrow 3\text{NO}_2$
- (iv) $\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$

i.e., some steps are bimolecular, and one unimolecular.

We may now consider the rate expressions of simple homogeneous reactions.

XV.4. First Order Kinetics. A reaction of the first order is represented as



where X is the reactant and Y the product. The rate of the reaction will be directly proportional to the concentration, i.e.,

$$\frac{-dC}{dt} = kC \quad \dots (XV.3)$$

in which C is the concentration of the reactant at any time t and k is a constant, called the *velocity constant* or *specific reaction rate*.

Rewriting,
$$\frac{-dC}{C} = k dt$$

On integration,
$$-\ln C = kt + z \text{ (constant).}$$

If at the start of the reaction, the initial concentration of the reactant is C_0 , then we have at $t = 0$, $C = C_0$.

Substituting,
$$-\ln C_0 = z$$

i.e.,
$$-\ln C = kt - \ln C_0$$

Hence
$$\ln \frac{C_0}{C} = kt, \text{ or } \frac{C}{C_0} = e^{-kt}$$

or
$$C = C_0 e^{-kt} \quad \dots (XV.4)$$

The concentration (C) therefore diminishes exponentially with time.

The rate equation may also be conveniently expressed in an alternative form, by expressing the rate in terms of the product. When x moles per unit volume of product Y is formed from the reactant, the concentration of the reactant is $a-x$, when a is the initial concentration of the reactant. So,

$$\frac{dx}{dt} = kC = k(a-x)$$

i.e.,
$$\frac{dx}{a-x} = k dt$$

On integration,
$$-\ln(a-x) = kt + z' \text{ (constant)}$$

When $t = 0$, $x = 0$, hence $-\ln a = z'$

$$\therefore -\ln(a-x) = kt - \ln a$$

i.e.,
$$\left. \begin{aligned} k &= \frac{1}{t} \ln \frac{a}{a-x} \\ x &= a(1 - e^{-kt}) \end{aligned} \right\} \quad \dots (XV.5)$$

or

It is obvious that equation XV.4 and XV.5 are the same.

Even when the initial concentration a is not known but the concentrations at two intervals t_1 and t_2 are known, the rate equation can be derived. If x_1 and x_2 are the concentrations of product at time t_1 and t_2 , then the corresponding concentrations of reactants would be $(a-x_1)$ and $(a-x_2)$. We can then write,

$$kt_1 = \ln \frac{a}{a-x_1} \quad \text{and} \quad kt_2 = \ln \frac{a}{a-x_2}$$

$$\therefore k(t_2 - t_1) = \ln \frac{a-x_1}{a-x_2}, \quad \text{or} \quad k = \frac{1}{t_2 - t_1} \ln \frac{a-x_1}{a-x_2} \quad \dots (XV.6)$$

Some interesting characteristics of the first order reactions are :

(i) In a first order reaction, $C = C_0 e^{-kt}$; the reaction cannot be complete. For C would become zero only at infinite time t .

(ii) The quantity $\frac{a}{a-x}$ (or $\frac{C_0}{C}$) is a ratio of concentrations, so its value will be the same whatever units are employed to express the concentrations, e.g., moles per litre, gms per c.c., partial pressures etc. It follows that the velocity constant k ($= \frac{1}{t} \ln \frac{a}{a-x}$) will have the dimension of reciprocal time, sec^{-1} .

(iii) The equation (XV.5) is $\ln(a-x) = -kt + \ln a$
or $\log(a-x) = -(k/2.303)t + \log a$.

If $\log(a-x)$ is plotted graphically against time, it would give a straight line. So when a plot constructed from experimental values of $(a-x)$ and t is found to be linear, the reaction is of first order. The slope of the line is $-k/2.3$, from which the velocity constant k is known.

(iv) The time required for half the reactant to change can be easily evaluated. Let $t_{\frac{1}{2}}$ be the time required when $x = a/2$.

$$\text{Then } t_{\frac{1}{2}} = \frac{1}{k} \ln \frac{a}{a-x} = \frac{1}{k} \times 2.3 \log \frac{a}{a/2} = \frac{2.3 \log 2}{k} = \frac{0.693}{k}.$$

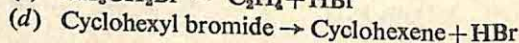
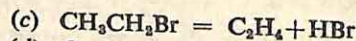
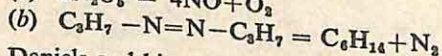
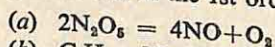
The period of half-decomposition is thus a constant for a given reaction and is independent of initial concentration. The time required is often called *half value period*, or '*half-life*' in the case of radioactive changes.

Not only half-value period, the time necessary to complete any definite fraction (ϕ) of the reaction is independent of the initial concentration in first order kinetics. For,

$$t_{\phi} = \frac{2.303}{k} \log \frac{a}{a-a\phi} = \frac{2.3}{k} \log \frac{1}{1-\phi} = \text{constant}.$$

The first order reactions are recognised from these characteristics.

Examples of first order reactions : Quite a number of homogeneous gaseous reactions have been found to be of the first order. The thermal dissociation of nitrogen pentoxide, acetone, azo-compounds, aliphatic ethers follow first order kinetics. The same is also found in the conversion of N-chloroacetanilide into p-chloroacetanilide (Blanksma, 1902); the individual radioactive changes are also of the 1st order.



Daniels and his co-workers studied the decomposition of N_2O_5 in the gas-phase as also in solution in solvents like carbon tetrachloride. In the gas-phase, the rate of reaction is followed by pressure measurements. The initial pressure of the gas is known and subsequently the total pressure at different time intervals were measured. From these measurements, with a knowledge of equilibrium constant of $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, the amount of undecomposed N_2O_5 corresponding to $(a-x)$ at different times were known. The values were substituted in equation (XV.5) and the velocity constant k was found out. The constancy of k as shown in the table below confirms the 1st order character of the reaction :

DECOMPOSITION OF N_2O_5 (45°C)*

Time in sec.	p (mm)	$k \times 10^4$ (sec. ⁻¹)	Time in sec.	p (mm)	$k \times 10^4$ (sec. ⁻¹)
0	348.4	—	4800	33	4.75
1200	185	4.81	6000	18	4.51
2400	105	4.78	7200	10	5.15
3600	78	4.84	8400	5	5.90

*F, Daniels, Chemical kinetics (1938), p. 9.

Daniels and Eyring studied the same decomposition in CCl_4 solvent. The progress of reaction was followed by measuring the evolved oxygen with time. Oxygen being insoluble in CCl_4 escaped from the solution ; other oxides of nitrogen remained in solution.

Since two molecules of N_2O_5 on decomposition liberates one molecule of oxygen. If V and V_∞ denote the volumes of oxygen given out at any time t and at the completion of reaction, then $(V_\infty - V)$ is the amount of undecomposed N_2O_5 at time t . It is easily seen,

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V},$$

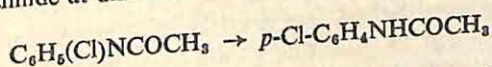
provided it is of the 1st order. Substitution of experimental data revealed a constancy in the value of k , confirming first order kinetics.

TABLE : DECOMPOSITION OF N_2O_5 IN CCl_4 SOLUTION (30°C)

Time (sec.)	$(V_\infty - V)\text{c.c.}$	$\log (V_\infty - V)$	$k (\text{sec}^{-1})$
0	84.85	1.9287	—
2400	69.20	1.8401	0.000085
4800	57.20	1.7574	0.000082
7200	47.15	1.6735	0.000081
9600	39.00	1.5911	0.000081
12000	32.18	1.5076	0.000081

The plot of $\log (V_\infty - V)$ against time t gives a straight line as in Fig. (XV.1) and the value of k derived from the slope of the line agrees well with those recorded above.

The conversion N-chloroacetanilide to *p*-chloroacetanilide has also been completely studied and found to be of the first order. The reaction was followed by estimating the reactant N-chloroacetanilide at different time intervals with KI.



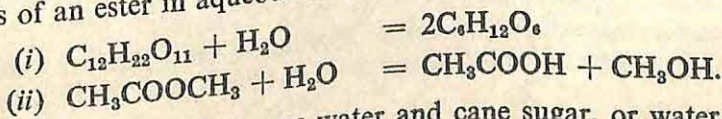
N-chloro compound liberates iodine from KI which is titrated with standard thiosulphate. The para-chloro compound does not liberate iodine from potassium iodide. The titre value gives the amount of $(a-x)$ at any time t . The initial concentration (a) is also expressed in terms of the same titre. The experimental values are given in the table below. The value of k was calculated for 1st order kinetics.

TABLE : CONVERSION OF N-CHLOROACETANILIDE INTO *p*-CHLOROACETANILIDE

Time (t , sec.)	$(a-x)$	$k \times 10^5 (\text{sec}^{-1})$
0	49.3	—
3600	35.6	9.03
7200	25.75	9.03
10800	18.5	9.07
21600	7.3	8.84

The constancy of k confirms the 1st order character of the reaction.

XV.5. Pseudo-Unimolecular Reactions. There are a number of reactions which follow the first order kinetics though more than one kind of chemical substances are involved in the reaction. Common examples are the inversion of cane sugar, hydrolysis of an ester in aqueous solution :



In such reactions, two substances water and cane sugar, or water and ester take part, but the rate of reaction is experimentally observed to depend only on the

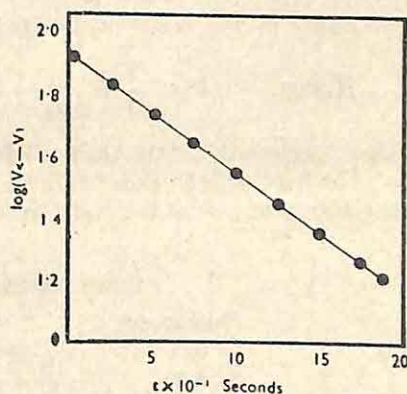


FIG. XV.1
Decomposition of N_2O_5 in CCl_4 soln

concentration of cane-sugar or the ester. It is normally expected that rate equations would be

$$(i) \frac{-dc}{dt} = kC_{\text{sugar}} \cdot C_{\text{H}_2\text{O}} \quad \text{and} \quad (ii) \frac{-dc}{dt} = kC_{\text{ester}} C_{\text{H}_2\text{O}}$$

But in such reactions, water is present relatively in such large excess that even if the reaction is complete, the concentration of water would virtually remain

constant. So that, $\frac{-dc}{dt} = kC_{\text{sugar}} \cdot C_{\text{H}_2\text{O}} = k'C_{\text{sugar}}$. The reaction rate is then

solely determined by the concentration of the cane-sugar (or the ester). As such these reactions follow first order kinetics. Such reactions since old days have been mentioned in literature as *pseudo unimolecular reactions*.

The same reactions, when carried out in non-aqueous media to which small quantities of water are added, are observed to depend upon the first power of concentration of water as well. In such conditions, the reaction behaves as one of the second order.

The progress of the inversion of cane sugar with time is followed polarimetrically. Cane-sugar solution rotates the plane of polarisation to the right, whereas the mixture of glucose and laevulose produced has a rotation to the left. If α_0 , α_t and α_∞ be the angles of rotation with proper signs at the beginning, at time t and at the completion of the reaction (i.e., after a very long time) respectively, then

$\alpha_0 - \alpha_\infty$ is proportional to the initial concentration a ,

and

$\alpha_0 - \alpha_t$ is proportional to the amount reacted, i.e., x .

$$\text{Hence} \quad k = \frac{1}{t} \ln \frac{\alpha_0 - \alpha_\infty}{(\alpha_0 - \alpha_\infty) - (\alpha_0 - \alpha_t)} = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}.$$

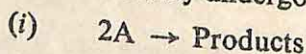
The experimental data (table below) have established the validity of this relation, i.e., the first order. The reaction is carried out in presence of an acid whose concentration however remains constant throughout.

TABLE : INVERSION OF SUCROSE (25°C, 0.9 M HCl)

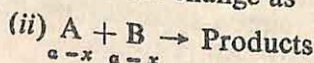
Time in min	α_t	$\alpha_t - \alpha_\infty$	$k \times 10^2$
0.0	+24.09	+34.83	—
18.0	17.73	28.47	1.117
36.8	12.40	23.14	1.112
46.0	10.02	20.76	1.113
56.0	7.80	18.54	1.113
∞	-10.74	—	—

Harcourt and Esson (1866) showed that the reduction of potassium permanganate with a great excess of oxalic acid follows the first order kinetics and is governed by equation (XV.5); the concentration of oxalic acid virtually remains unaffected.

XV.6. Second Order Kinetics. A reaction will be of the second order when the reaction rate would depend upon the product of two concentrations. This may arise in two ways : either a single substance may undergo a change as



or two reactants may participate in the change as



If the two substances have the same initial concentration (a) and if x denotes the concentration of the reactants which disappears in time t , then the rate will be

$$\frac{dx}{dt} = k(a-x)^2 \quad \dots (XV.7)$$

Rearranging,
$$\frac{dx}{(a-x)^2} = kdt$$

Integrating,
$$\frac{1}{a-x} = kt + z \text{ (constant)}$$

when $t = 0, x = 0, \therefore \frac{1}{a} = z$

Hence,
$$\frac{1}{a-x} - \frac{1}{a} = kt$$

The velocity constant,
$$k = \frac{x}{at(a-x)} \quad \dots \text{(XV.8)}$$

When the initial concentrations of the two substances participating are different, say a and b , then the rate is given by

$$\frac{dx}{dt} = k(a-x)(b-x) \quad \dots \text{(XV.9)}$$

where x is the amount of any reactant transformed in time t .

Rewriting,
$$\frac{dx}{(a-x)(b-x)} = kdt$$

or
$$\frac{1}{a-b} \left[\frac{1}{b-x} - \frac{1}{a-x} \right] dx = kdt$$

Integrating,
$$\frac{1}{a-b} [-\ln(b-x) + \ln(a-x)] = kt + z \text{ (constant)}$$

or
$$\frac{1}{a-b} \ln \frac{a-x}{b-x} = kt + z$$

When $t = 0, x = 0$, therefore
$$\frac{1}{a-b} \ln \frac{a}{b} = z$$

Substituting
$$\frac{1}{a-b} \ln \frac{a-x}{b-x} - \frac{1}{a-b} \ln \frac{a}{b} = kt$$

or
$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)} \quad \dots \text{(XV.10)}$$

or
$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad \dots \text{(XV.11)}$$

It may be also written as
$$t = \frac{2.303}{k(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

which means that the plot of $\log \frac{b(a-x)}{a(b-x)}$ against t for such a reaction

would be linear, a fact which has been corroborated by experimental observation in many second order reactions. The straight line would pass through the origin and from its slope $2.303/k(a-b)$, the velocity constant would be obtained.

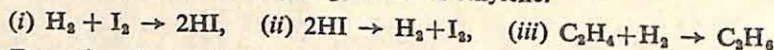
The value of k would depend on the units employed in expressing a and b , for, the magnitudes of $(a-b)$ would depend on the units used.

In a second order reaction where the two initial concentrations are the same, the equation (XV.8) is applicable. The half value period ($t_{\frac{1}{2}}$) for such a reaction is given by

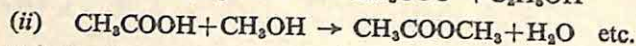
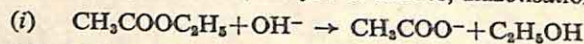
$$t_{\frac{1}{2}} = \frac{x}{ak(a-x)} = \frac{a/2}{a.k.a/2} = \frac{1}{ak}$$

i.e., the time required for half the amount of reactant to undergo the change is inversely proportional to the initial concentration (a), whereas in first order reactions $t_{\frac{1}{2}}$ is constant.

Examples of Second Order Reactions. A large number of reactions both in gas and in liquid phases have been found to be of the second order. The hydrogen-iodine reaction as also the decomposition of hydrogen iodide have both been studied thoroughly and observed to follow the second order kinetics. So also is the hydrogenation of ethylene.



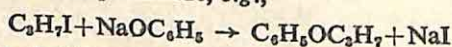
Examples of second order reactions are found in the alkaline hydrolysis of ester, the esterification of acids, alkaline hydrolysis of amides, diazotisation of many amines etc.



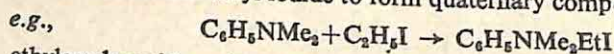
In following the kinetics of alkaline hydrolysis of esters, known concentrations of ester (a) and alkali (b) are taken in a mixture. The amount of alkali consumed in the reaction at different times is followed by measuring the conductance of the solution or by withdrawing samples and titrating the same with standard acid. Thus x is known and hence ($a-x$) and ($b-x$) are also known. The velocity constant k is then calculated with equation (XV.11).

Of the other interesting second order reactions in solution carefully studied may be mentioned

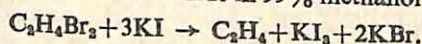
(a) alkyl iodides with sodium phenoxide, e.g.,



(b) tertiary amine and alkyl iodide to form quaternary compounds :

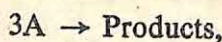


(c) ethylene bromide and potassium iodide in 99% methanol :



It was found to follow the second order kinetics as, $k_2 = \frac{1}{t(3a-b)} \ln \frac{b(a-x)}{a(b-3x)}$.

XV.7. Third Order Kinetics. Only a few third order reactions are definitely known and most of these are concerned with nitric oxide. In the simplest case of a third order reaction, we have



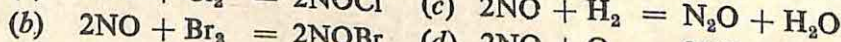
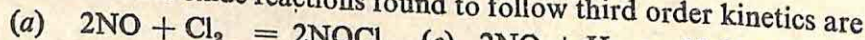
So that,

$$\frac{dx}{dt} = k(a-x)^3, \quad \text{or,} \quad \frac{dx}{(a-x)^3} = k dt$$

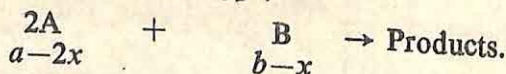
Integrating,

$$k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right] \quad \dots \text{(XV.12)}$$

But the nitric oxide reactions found to follow third order kinetics are



That is, these reactions are of the type,



If a and b are the initial concentrations of A and B and if x is the amount of B changed in time t , then the concentrations of reactants at time t are ($a-2x$) and ($b-x$).

Hence,

$$\frac{dx}{dt} = k(a-2x)^2(b-x) \quad \dots \text{(XV.13)}$$

This, on integration by the method of partial fractions, gives

$$k = \frac{1}{t} \cdot \frac{1}{(2b-a)^2} \left[\frac{2x(2b-a)}{a(a-2x)} + \ln \frac{b(a-2x)}{a(b-x)} \right] \quad \dots \text{(XV.14)}$$

The kinetics of the NO-reactions mentioned above have actually been observed to obey this relation.

In solution, a third order reaction has been observed in the mutarotation of tetramethyl glucose in presence of pyridine and phenol. (J. Am. Chem. Soc. 1952, 74, 2534).

Reactions of fourth or higher order seem to be improbable and no reaction is definitely known to have a higher order. In general, a reaction of the n th order, where all the initial concentrations are the same, has a reaction rate,

$$\frac{dx}{dt} = k(a-x)^n$$

On integration,
$$k = \frac{1}{t(n-1)} \left\{ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right\} \dots \text{(XV.15)}$$

This equation is applicable for all orders except when $n = 1$. Thus,

when $n = 3$,
$$k = \frac{1}{2t} \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\} \quad (\text{same as eqn. XV.12})$$

When $n = 3/2$;
$$k = \frac{2}{t} \left\{ \frac{1}{(a-x)^{1/2}} - \frac{1}{a^{1/2}} \right\} \text{ etc.}$$

The half-value period of the n th order reaction of this type will be given by,

$$\begin{aligned} t_{1/2} &= \frac{1}{k} \frac{1}{(n-1)} \left\{ \frac{1}{(a-a/2)^{n-1}} - \frac{1}{a^{n-1}} \right\} \\ &= \frac{2^{n-1}-1}{k(n-1)} \cdot \frac{1}{a^{n-1}} = \frac{k'}{a^{n-1}} \dots \text{(XV.16)} \end{aligned}$$

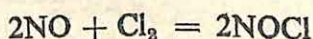
That is, half-value period is inversely proportional to the $(n-1)$ th power of the initial concentration.

XV.8. Specific Reaction Rate. The velocity constant, k , used in the rate equations is equivalent to the reaction rate (dx/dt) when all the reactants are at unit concentrations. The reaction rate is always expressed in moles per litre per second. The expressions for the reaction rates of different orders have different powers of concentration. The units of k must therefore be different for different orders.

For a first order reaction $k = (dx/dt)/C$, hence the dimensions of k is moles per litre per sec./moles per litre, i.e., sec^{-1} . For a second order reaction $k = (dx/dt)/C^2$, hence k 's units would be litres mole $^{-1}$ sec $^{-1}$. In general, the units for k for a reaction of n th order would be given by,

$$\frac{\text{moles per litre per sec.}}{(\text{moles per litre})^n} \quad \text{i.e., litres}^{n-1} \text{ moles}^{1-n} \text{ sec}^{-1}.$$

In describing the rate of reaction or the specific reaction rate, when more than one substance take part as reactant, it is necessary to mention the reactant to which the rate refers. Thus in the reaction,



the rates may be expressed in any one of the following :

$$\frac{dC_{\text{NOCl}}}{dt} = k_1 C_{\text{NO}}^2 C_{\text{Cl}_2}; \quad \frac{-dC_{\text{Cl}_2}}{dt} = k_1' C_{\text{NO}}^2 C_{\text{Cl}_2}; \quad \frac{-dC_{\text{NO}}}{dt} = k_1'' C_{\text{NO}}^2 C_{\text{Cl}_2}$$

Remembering that for every mole of chlorine two moles of NO react and two moles of NOCl are produced, it is obvious

$$k_1 = 2k_1' = k_1''.$$

XV.9. Determination of the Order of a Reaction. The different methods used in the determination of the order of a reaction may be considered now. In every method, it is, of course, necessary to determine the concentration of a reactant or a product at various time intervals.

Method of Integration. This method has already been described in connection with the alkali hydrolysis of esters, or the inversion of cane sugar. The amounts of products (x) at different time intervals (t) are first experimentally determined. These values are then introduced into the different rate equations in their integrated forms, such as equation (XV.5), (XV.8), (XV.11) etc. until a constant value for the specific reaction rate is obtained. The equation which satisfies this indicates the order of the reaction. For simple homogeneous reactions, this method of trial with rate equations is quite satisfactory and often employed. But for complex reactions, the method may lead to erroneous conclusions.

Method of Half-value Period. The time at which half of the reactant would disappear is the half-value or half-life period ($t_{\frac{1}{2}}$). We have seen that the half-value period is constant for a 1st order reaction, and that the same is inversely proportional to the initial concentration for a 2nd order reaction, etc. For a reaction of the n th order, (eqn. XV.16).

$$t_{\frac{1}{2}} = \frac{k'}{a^{n-1}} \quad \dots \text{(XV.16)}$$

Suppose two experiments are carried out with initial concentrations a and a' , then their half-value periods would be related as

$$\frac{t_{\frac{1}{2}}}{t'_{\frac{1}{2}}} = \left(\frac{a'}{a}\right)^{n-1}, \text{ or } (n-1) \log \frac{a'}{a} = \log \frac{t_{\frac{1}{2}}}{t'_{\frac{1}{2}}}$$

$$\text{or } n = 1 + \frac{\log t_{\frac{1}{2}}/t'_{\frac{1}{2}}}{\log a'/a} \quad \dots \text{(XV.17)}$$

Plotting the concentrations against time, $t_{\frac{1}{2}}$ and $t'_{\frac{1}{2}}$ can be easily obtained, so the order n for the reaction can be calculated. Sometimes plots of $t_{\frac{1}{2}}$ vs $1/a$, $t_{\frac{1}{2}}$ vs $1/a^2$ etc. are also tried, and that which gives a linear plot would indicate the order.

Differential Method. This method is also called van't Hoff's method as it was introduced by him. The rate of a reaction of the n th order is given by

$$-\frac{dC}{dt} = kC^n$$

In two experiments with initial concentrations C_1 and C_2 , we may write

$$\frac{-dC_1}{dt} = kC_1^n \quad \frac{-dC_2}{dt} = kC_2^n$$

$$\text{or } \log \left(\frac{-dC_1}{dt} \right) = \log k + n \log C_1; \log \left(\frac{-dC_2}{dt} \right) = \log k + n \log C_2$$

$$\text{Subtracting, } n = \frac{\log \left(\frac{-dC_1}{dt} \right) - \log \left(\frac{-dC_2}{dt} \right)}{\log C_1 - \log C_2} \quad \dots \text{(XV.18)}$$

The procedure is to plot concentration vs time for two experiments with different initial concentrations. The slopes ($-dC/dt$) at a given time interval is measured in both cases. Using these values in the above equation, n is determined.

Sometimes in the case of simple reactions, the rate ($-dC/dt$) is obtained from the conc.-time curve, for about 20–30% of the reaction. Then $\log (-dC/dt)$ is plotted against $\log C$ separately. The slope of the linear plot gives the value of n , the reaction order.

This method can also be applied to the evaluation of the order when more

than one reactant are involved. Suppose the reaction is of n_1 th order with respect to reactant A and n_2 th order with respect to reactant B. Then,

$$\text{Reaction rate} = k C_A^{n_1} C_B^{n_2}$$

Two sets of experiments are to be performed. In one set, the concentration of B (C_B) is to be always kept constant while $(-dC/dt)$ should be measured for different initial concentration of A. These, with the help of equation (XV.18), would give the value of n_1 . Next, in the second set of experiments, the concentration of A shall remain constant, and similar process should be repeated with different initial concentrations of B. From these the value of n_2 would be available. Thus the net order of the reaction ($n_1 + n_2$) would be known.

The conc.-time curves are to be plotted for experiments with different initial concentrations. The dC/dt is then evaluated from each curve after the lapse of the same time period from the start of the reaction.

Example : In the reaction between H_2 and NO, the following data were recorded :

At const. pressure of hydrogen, with $p_{NO} = 300$; $\frac{-dp}{dt} = 1.03$ mm/sec.

and with $p_{NO} = 152$, $\frac{-dp}{dt} = 0.25$ mm/sec.

Hence reaction order with respect to NO is,

$$n_{NO} = \frac{\log 1.03 - \log 0.25}{\log 300 - \log 152} = 2.1 \approx 2$$

Again when pressure of NO was kept constant,

with $p_{H_2} = 205$ mm, $\frac{-dp}{dt} = 1.10$ mm/sec.

with $p_{H_2} = 147$ mm, $\frac{-dp}{dt} = 0.79$ mm/sec.

$$\therefore n_{(H_2)} = \frac{\log (1.10) - \log (0.79)}{\log 205 - \log 147} = 1.0$$

The reaction is of the second order with respect to NO and of the first order with respect to H_2 ; the overall reaction is of the third order.

$$\text{i.e.,} \quad \frac{-dC}{dt} = k C_{NO}^2 C_{H_2}$$

Isolation Method. This method which was introduced by Ostwald (1902) involves an artificial simplification of the order of a reaction by using a large excess of the reactants except one. Suppose a reaction is of α th order with respect to A, and β th order with respect to B. Now if a large excess of B is used so that its concentration throughout the reaction virtually remains constant, the reaction rate will be given by

$$\frac{-dC_A}{dt} = k (C_A)^\alpha (C_B)^\beta = k' (C_A)^\alpha$$

The apparent order (α) may be determined by any of the three methods described above. The value of β can similarly be obtained by using a large excess of the reactant A. Care should be exercised in using this method, for if the reaction is a complex one excess of some components may alter the mechanism of the process and in consequence erroneous results may be obtained.

The methods so far discussed are suitable for simple and direct reactions, where reaction rates are simple power function of the concentrations. But most reactions are of a complex nature, occurring in stepwise fashion, and the application of these methods would not be of much help. The complex nature of a reaction is often indicated by plotting $\log(-dC/dt)$ vs $\log C$ in the differential method

when it gives a curve instead of a straight line. Complications also arise when several reactions occur at the same time. These are known as *simultaneous reactions*. The simultaneous reactions may be divided into three classes :

(1) *Side reactions* (2) *Consecutive reactions* (3) *Opposing reactions*.

XV.10. Side Reactions. When a reactant (A) gives rise to more than one independent product, it is a case of side reactions.



Let a be the initial concentration of A and x be the amount disappeared in time t partly as B and partly as C. Then, suppose,

$$\frac{dx}{dt} = \text{rate of formation of B and C together.}$$

$$\frac{dy}{dt} = \text{rate of formation of B} = k_1(a-x)^n$$

$$\frac{dz}{dt} = \text{rate of formation of C} = k_2(a-x)^{n'}$$

At any moment, we have the relation,
$$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt}$$

Assuming 1st order for both the reactions ($n = n' = 1$),

$$\frac{dx}{dt} = k_1(a-x) + k_2(a-x) = (k_1 + k_2)(a-x)$$

Integrating, we have, $\frac{1}{t} \ln \frac{a}{a-x} = k_1 + k_2 = k$ (say) ... (XV.18)

The value of k can be found out by following the concentration changes in A with time. But the separate evaluation of k_1 and k_2 needs a further relation between them.

Remembering that at any moment,

$$\frac{\text{rate of formation of B}}{\text{rate of formation of C}} = \frac{k_1(a-x)}{k_2(a-x)} = \frac{k_1}{k_2} = z \text{ (say).}$$

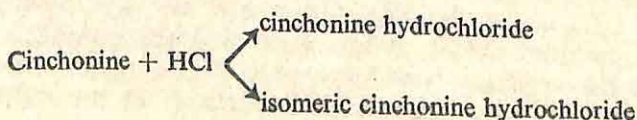
But the ratio of the rates is the same as the amounts of B and C at any stage.

$$\therefore \frac{\text{amount of B at any stage}}{\text{amount of C at the same stage}} = k_1/k_2 = z \quad \dots \text{ (XV.19)}$$

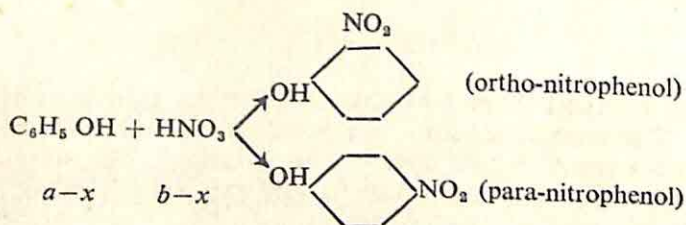
The estimation of B and C at some suitable stage, say at the end of the reaction, would give the value of z . Thus, k and z are both experimentally measured. $k = k_1 + k_2$ and $z = k_1/k_2$; hence k_1 and k_2 , the individual reaction rate constants, can be evaluated.

The ratio of amounts of B and of C at any time interval would be the same, provided the orders of the two parallel reactions be the same. This is known as Wegscheider's Test for side reactions distinguishing them from opposing or consecutive reactions. Wegscheider test will not be applicable if order of the two side reactions be not the same.

Examples : (a) Wegscheider had shown that when HCl was added to cinchonine, ordinary hydrochloride and its isomer were formed. The amounts of the two were in constant ratio independent of the time chosen for measurement.



(b) Nitration of phenol gives two products ortho-and para- nitrophenols,



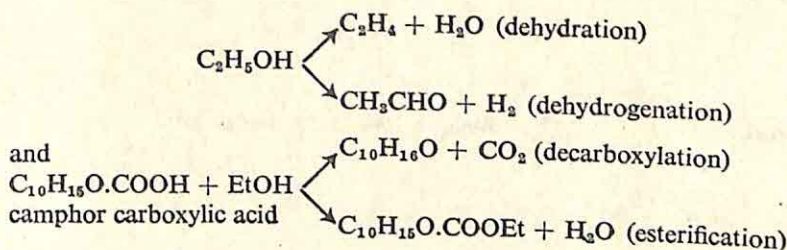
The rate of formation of ortho-product : $\frac{dy}{dt} = k_1 (a-x) (b-x)$

The rate of formation of para-product : $\frac{dz}{dt} = k_2 (a-x) (b-x)$

$$\therefore \frac{\text{Amount of } y}{\text{Amount of } z} = \frac{dy/dt}{dz/dt} = \frac{k_1 (a-x) (b-x)}{k_2 (a-x) (b-x)} = \frac{k_1}{k_2} = z \text{ (constant)}$$

Thus, the Wegscheider test is applicable.

Other well studied examples are the decomposition of ethanol vapour, of camphor-carboxylic acid in alcoholic solution, etc.



Autocatalytic Reactions. Sometimes one of the products of a reaction is capable of accelerating the rate of the reaction. Such a reaction is called an *autocatalytic* reaction. Thus, in the hydrolysis of esters, the acid produced in the reaction also catalyses the reaction. In the hydrolysis of ethyl acetate catalysed by acetic acid, let the initial concentration of ester be a and of acetic acid be b ; suppose x is the amount of ester hydrolysed at time t , then

$$\frac{dx}{dt} = kb(a-x) + kx(a-x)$$

It will be seen later in homogeneous catalysis, the rate is proportional to the concentration of the catalyst as well. Rewriting,

$$\frac{dx}{dt} = k(a-x) (b+x)$$

On integration and remembering when $t = 0$, $x = 0$, we have $k = \frac{1}{t(a+b)} \ln \frac{a(b+x)}{b(a-x)}$.

This has been experimentally confirmed.

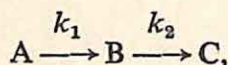
If the initial catalyst be an acid other than acetic acid, then

$$\frac{dx}{dt} = k_1(a-x)b + k_2(a-x)x = (k_1b + k_2x) (a-x)$$

This, on integration gives, $k_1b + k_2a = \frac{1}{t} \ln \frac{a(k_1b + k_2x)}{k_1b(a-x)}$

Other common examples of autocatalysis is found in the oxidation of oxalic acid by KMnO_4 soln in which the product Mn^{++} ions act as catalyst, the reaction becoming faster and faster with time. Again, the dissolution of copper by nitric acid is initially slow but as nitrous acid is produced the rate is much enhanced, for, the latter is a strong catalyst for the process.

XV.11. Consecutive Reactions. Consecutive reactions may be represented as



that is, the reactions proceed from reactants to products through one or more intermediate stages. The overall reaction is a result of several consecutive steps. Every stage has its own reaction rate and velocity constant. The simplest case is one in which there are only two consecutive stages and the two reactions are of the 1st order with specific reaction rates k_1 and k_2 .

Suppose c_0 is the initial concentration of A, and let c_1 , c_2 and c_3 denote the concentrations of A, B and C respectively at any time t . We have, therefore,

$$c_0 = c_1 + c_2 + c_3$$

and, the rate of disappearance of A, $-\frac{dc_1}{dt} = k_1 c_1$.

Hence, using eqn. XV.4,

$$c_1 = c_0 e^{-k_1 t} \quad \dots \text{(XV.20)}$$

Since the rate of formation of B is given by $k_1 c_1$ and the rate of decomposition of B into C is given by $k_2 c_2$, the rate at which B accumulates in the system is given by,

$$\frac{dc_2}{dt} = k_1 c_1 - k_2 c_2$$

That is, $\frac{dc_2}{dt} + k_2 c_2 = k_1 c_1 = k_1 c_0 e^{-k_1 t}$

$$\text{or } e^{k_2 t} \cdot \frac{dc_2}{dt} + e^{k_2 t} \cdot k_2 c_2 = k_1 c_0 e^{-k_1 t} \cdot e^{k_2 t} = k_1 c_0 e^{(k_2 - k_1)t}$$

$$\text{Integrating, } c_2 e^{k_2 t} = \frac{k_1 c_0}{k_2 - k_1} e^{(k_2 - k_1)t} + z \text{ (constant)}$$

$$\text{When } t = 0, c_2 = 0, \therefore z = -\frac{k_1 c_0}{k_2 - k_1}$$

Hence

$$c_2 e^{k_2 t} = \frac{k_1 c_0}{k_2 - k_1} [e^{(k_2 - k_1)t} - 1]$$

or

$$c_2 = \frac{k_1 c_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}] \quad \dots \text{(XV.21)}$$

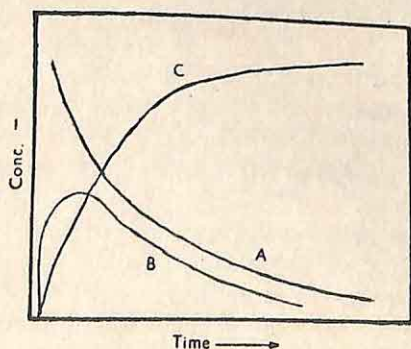


FIG. XV.2 Consecutive reaction,
 $A \rightarrow B \rightarrow C$

Starting with an initial concentration c_0 , the experimental determination of c_1 and c_2 at any time t would enable one to evaluate k_1 and k_2 utilising equations (XV.20 and 21).

Equation (XV.20) shows that the concentration of A falls exponentially, whereas the amount of C will rise until it approaches that of A. The concentration of B will first increase and then it will decrease, showing a maximum. This is illustrated in Fig. XV.2.

When maximum concentration of B is reached, $dc_2/dt = 0$. Therefore differentiating eqn. (XV.21),

$$\frac{dc_2}{dt} = \frac{k_1 c_0}{k_2 - k_1} \left[-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} \right] = 0.$$

or $k_2 e^{-k_2 t} = k_1 e^{-k_1 t}$; i.e., $k_1/k_2 = e^{(k_1 - k_2)t}$

or $t = \frac{\ln k_1 - \ln k_2}{k_1 - k_2}.$

This is experimentally verified.

When one of the reaction is very fast compared to the other, the reaction will follow simply the kinetics of the slower process. Since

$c_3 = c_0 - c_1 - c_2$, substituting from eqns. XV.20 and 21, we have,

$$c_3 = c_0 \left[1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} - \frac{k_1}{k_1 - k_2} e^{-k_2 t} \right] \quad \dots \text{(XV.22)}$$

When $k_2 \gg k_1$,

$$c_3 = c_0(1 - e^{-k_1 t})$$

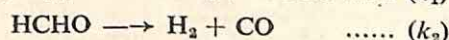
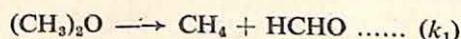
and when $k_1 \gg k_2$,

$$c_3 = c_0(1 - e^{-k_2 t})$$

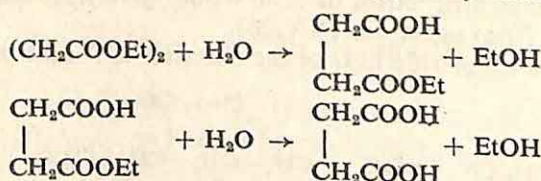
$\dots \text{(XV.23)}$

which shows that the overall process will have a simple first order kinetics. To illustrate, we may cite the following reactions.

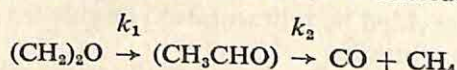
(a) The decomposition of dimethyl ether occurs in two stages :



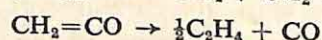
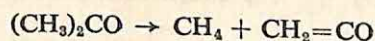
(b) The acid hydrolysis of ester of dibasic acids, e.g., diethyl succinate,



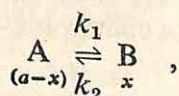
(c) The decomposition of ethylene oxide is also a consecutive process :



(d) The pyrolysis of acetone also takes place through the intermediate stage of ketene, as



XV.12. Opposing Reactions. The other type of simultaneous reaction is the opposing or reversible reaction. In a reversible process, if the equilibrium is far away from one end, then the reaction may be found to follow a simple reaction rate at least in the beginning of the reaction, the very slow reverse process being ignored. But when the reaction rates are appreciable for both the forward and the reverse processes, the kinetics must take into consideration both the processes. The simplest case is when both the forward and the reverse reactions are of the first order, as



k_1 and k_2 being the specific reaction rates in the two opposite directions. Starting with pure A of concentration a , let x be the concentration of B after time t , then

$$\begin{aligned} \frac{dx}{dt} &= k_1(a-x) - k_2x \\ &= k_1a - (k_1 + k_2)x. \end{aligned}$$

Integrating,
$$t = -\frac{1}{k_1+k_2} \ln (k_1 a - k_1 + k_2 x) + z$$

When $t = 0, x = 0, \therefore z = \frac{1}{k_1+k_2} \ln k_1 a$

$$\therefore t = \frac{1}{k_1+k_2} \ln \frac{k_1 a}{k_1 a - (k_1 + k_2)x}$$

or
$$k_1 + k_2 = \frac{1}{t} \ln \frac{k_1 a}{k_1 a - k_1 + k_2 x} \quad \dots (XV.24)$$

If the eqm. constant of the reaction is K , then $K = k_1/k_2 \quad \dots (XV.25)$

From these two relations, both k_1 and k_2 can be evaluated.

An alternative expression is sometimes useful. Suppose x_e is the concentration of B at equilibrium, then

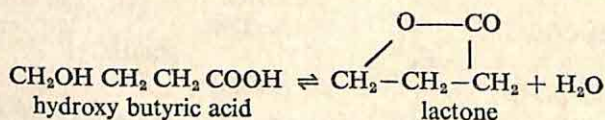
$$\frac{dx}{dt} = k_1(a-x_e) - k_2 x_e = 0, \quad \text{or} \quad k_2 = \frac{k_1(a-x_e)}{x_e} \quad \dots (XV.26)$$

Hence
$$\frac{dx}{dt} = k_1(a-x) - k_2 x = k_1(a-x) - \frac{k_1(a-x_e)}{x_e} \cdot x = \frac{k_1 a}{x_e} (x_e - x)$$

Integrating,
$$k_1 = \frac{x_e}{at} \ln \frac{x_e}{x_e - x} \quad \dots (XV.27)$$

Measurement of x as a function of time would give the value of k_1 . The value of k_2 will be available from equation (XV.26).

Example of such a reversible first order reaction is found in the process :

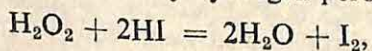


Other illustrations are provided by mutarotation of glucose and the conversion of ammonium thiocyanate to thiourea.

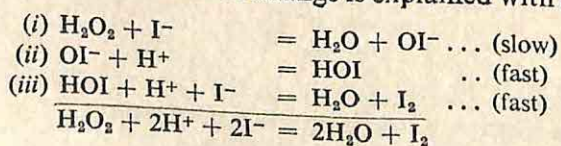
Reactions in which both the forward and the reverse processes are of the second order are also known, such as, the esterification of acids, hydrogen-iodine reaction etc.

XV.13. Steady State Concept : Complex Reactions. In the derivation of the rate equations in the preceding pages, it has been tacitly presumed that the reactants interact directly to produce the resultants. But in very few cases this actually happens ; in most reactions, they are quite complex in nature. The transformation occurs in quite a complicated fashion in several successive stages. To illustrate, some well-studied reactions may be cited.

The oxidation of hydroiodic acid by hydrogen peroxide,

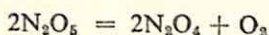


has been observed to follow second order kinetics, although three molecules are essentially required. The mode of change is explained with a three stage process:



The rate of transformation is different in different stages ; the changes in stages (ii) and (iii) are well-known to be practically instantaneous. The overall rate of reaction is thus dependent on the relatively slow process of stage (i).

Again, the decomposition of nitrogen pentoxide is



The process has been found to be of the first order though stoichiometrically two molecules of N_2O_5 are necessary for the change. The mechanism of the process as suggested by Ogg (1947) consists of the following steps.

- (i) $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$
- (ii) $\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$
- (iii) $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 + \text{NO}_2$ (slow)
- (iv) $\text{NO} + \text{N}_2\text{O}_5 = 3\text{NO}_2$

The third step (iii) is relatively slow compared to the other steps and the overall reaction is determined by the rate of this step.

It is thus seen that many reactions which appear to be quite simple are indeed very complex. The stoichiometric representation has no bearing either on the mechanism of transformation or on the order of the reaction observed. It is because of the step-wise changes involved in most reactions that reactions of higher orders are seldom met with and seem to be improbable. Even third order reactions are very few and only five or six reactions are definitely known to be of the third order.

In such stepwise complex reactions, *the overall reaction rate is determined by the slowest of the different steps*. The order of the reaction is the order of the slowest stage in the process. Further, most often the intermediates or unstable species produced in the stages, such as OI^- in hydroiodic acid oxidation, would have a short-lived transient existence. The concentrations of the intermediates at any time will be quite small and fixed. That is, the rate of formation of the intermediate

and the rate of its disappearance would be the same ; $\frac{-dc_{int}}{dt} = 0$. This

fact of a constant concentration of the intermediate unstable species is commonly known as *steady state concept*, and is of invaluable assistance in interpreting the mechanism of most reactions.

XV.14. Influence of Temperature on Reaction Rates : The Arrhenius Equation. Temperature has a profound influence on the reaction velocity. In homogeneous thermal reactions, for every ten degree rise in temperature, the velocity of reaction is doubled or trebled. The ratio, called temperature coefficient, is

$\frac{k_{t+10}}{k_t} \approx 2$ to 3. The enhancement of reaction rate is found with reactions in gaseous as well as in solution phases. Some typical data are given below.

TABLE : REACTION RATES AT DIFFERENT TEMPERATURES

(A) Decomposition of N_2O_5 (gas)		(B) Decomposition of CH_3CHO (gas)		(C) Reaction in alcoholic solution $\text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{ONa} \rightarrow \text{CH}_3\text{OC}_2\text{H}_5$	
Temp °C	$k \times 10^4 \text{ sec}^{-1}$	Temp °C	$k \text{ sec}^{-1} (\text{mole/lit}^{-1})$	Temp. °C	$k \times 10^5 \text{ litre/mol-sec.}$
25	0.34	460	0.035	0	5.6
35	1.35	518	0.343	6	11.8
45	4.98	538	0.80	12	24.5
55	15.0	563	2.14	24	100
65	48.7	592	4.96	30	208

Arrhenius (1889) showed that the velocity constant (k) of a chemical process increases exponentially with temperature for a large number of reactions, it was

observed that the plot of $\log k$ against $1/T$ gives a linear relation. He, therefore, suggested empirically the relation as

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \quad \dots (XV.29)$$

$$\text{or} \quad \ln k = \frac{-E}{RT} + \text{constant} \quad \dots (XV.30)$$

$$\text{i.e.,} \quad k = Ae^{-E/RT} \quad \dots (XV.31)$$

These are the different forms of what is commonly known as the Arrhenius equation, correlating temperature and specific reaction rate. 'A' is called the *frequency factor* and 'E' the *activation energy* of the reaction. These two quantities have definite values for any given reaction.

By measuring the velocity constant k and k' at two temperatures T and T' respectively, we have, from eqn. (XV.30),

$$\log k = -\frac{E}{2.303R} \cdot \frac{1}{T} + \log A$$

$$\log k' = -\frac{E}{2.303R} \cdot \frac{1}{T'} + \log A$$

$$\text{i.e.,} \quad \log k/k' = -\frac{E}{2.303R} \cdot \left[\frac{T' - T}{TT'} \right] \quad \dots (XV.32)$$

Hence the activation energy E is easily obtained.

Alternatively, a plot of $\log k$ against $\frac{1}{T}$ gives a straight line, as shown in Fig.

XV.3. The slope of such lines gives the value of $\frac{E}{2.303R}$, from which E is evaluated.

The intercept of the line would also enable one to find out the value of the frequency factor, A .

Now suppose k_1 and k_2 are the velocity constants in the two opposite directions of a reversible process at temp T . From eqn. (XV.30),

$$\ln k_1 = \frac{-E_1}{RT} + z_1 (\text{constant})$$

$$\text{and} \quad \ln k_2 = \frac{-E_2}{RT} + z_2 (\text{constant})$$

$$\text{Subtracting, } \ln \frac{k_1}{k_2} = \frac{(E_2 - E_1)}{RT} + z (\text{constant}), \quad z = z_1 - z_2.$$

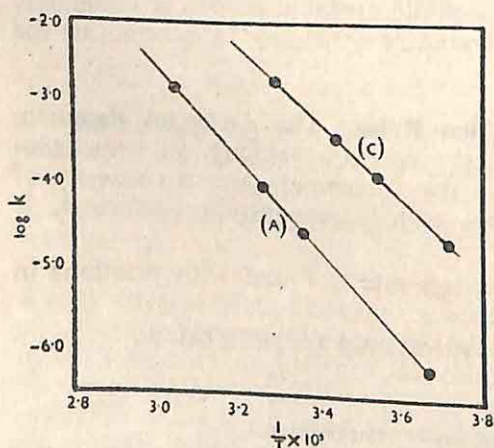


Fig. XV.3

But $\frac{k_1}{k_2} = K$, equilibrium constant of the reaction.

$$\text{Hence, } \ln K = \frac{E_2 - E_1}{RT} + z$$

where E_1 and E_2 are the activation energies of the two opposite processes.

$$\text{Hence, } \frac{\partial \ln K}{\partial T} = -\frac{(E_2 - E_1)}{RT^2} = \frac{E_1 - E_2}{RT^2} \quad \dots (XV.33)$$

$$\text{But from van't Hoff isochore, } \frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2} \quad \dots (XV.34)$$

where ΔH is the heat-change of the chemical process.

$$\text{Comparing, } \Delta H = E_1 - E_2.$$

It is obvious that E -terms in the Arrhenius equation must have units of energy. The heat of reaction of the process is the difference in the energy of activation of the two opposing changes.

Significance of activation energy, E . According to Arrhenius the molecules must acquire a certain critical energy before they would undergo chemical transformation. This means that before the chemical reaction can occur the molecule or molecules involved must be raised to a higher energy level *i.e.*, the molecules must be in an energy-rich or activated state before they can react. This may be made clear with the aid of a schematic diagram as in Fig. XV.4.

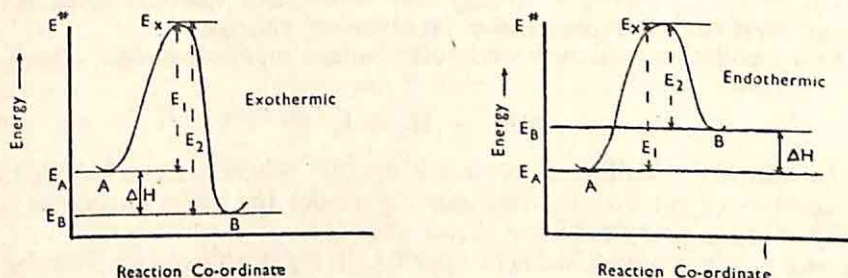


FIG. XV.4 Activation energy

The average energy of the reactant is represented by E_A and that of the resultant E_B . But even if E_A is greater than E_B the reactant A will not be straight-way transformed to the product B. There is a minimum energy level for the reaction denoted by E_X to which the reactant molecule must be raised in order to enable it to undergo the chemical change. The excess or additional energy ($E_X - E_A$) which the reactant must acquire in order to undergo transformation is the activation energy, E_1 . Molecules, having energy E_X or above, are said to be in *activated state* and such molecules only are fit for chemical reaction.

This idea of the activated-state (or activated complex formed from reactants) has been qualitatively presented in Fig. XV.4 plotting the energy of the system in relation to the *reaction co-ordinate*. The reaction co-ordinate is a measure of the approach of the reactant molecules towards the transformation. As the reactant molecules come together, their structural orientations, their internal vibrations, their relative internuclear distances etc. change and even they may make a transient association. The reaction co-ordinate is a measure of these physical variations which necessarily involve energy-changes of the system. It does not depend on a single internuclear distance but all internuclear distances and structural variations during the transformation into product molecules. It is not possible to give any quantitative value for the reaction co-ordinate. It merely gives a qualitative description of the conversion of reactants into products.

After the chemical transformation, the products will have the average energy E_B . Hence an amount of energy $(E_X - E_B) = E_2$ will be given out. If $E_2 > E_1$, the reaction is evidently exothermic as in Fig. XV.4 (I), whereas if $E_2 < E_1$, the reaction is endothermic.

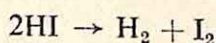
Moreover, if the reverse reaction $B \rightarrow A$ is followed, the molecules of B must reach the level E_X by acquiring energy E_2 and thus be activated to be transformed into A molecules. Then, on reaction, the excess energy E_1 will be given up by the activated species.

This concept that the molecules must possess the activation energy before they can undergo the chemical change has now been universally accepted for all realised and how the molecules behave during the transformation. In other words, molecules are converted into products is necessary. Attempts in the elucidation of the mechanism led to two theories, namely (i) collision theory and (ii) the transition state theory. We shall now briefly discuss these two theories.

XV.15. The Collision Theory. The collision theory is based on the concept that the reaction occurs when the reactant molecules, say A and B, come very close to

each other or collide. The collision between the reactant molecules is thus the first step in the process of a chemical transformation. The rate of reaction will naturally be proportional to the number of collisions per unit time between the reactant molecules. It will be presently shown that every collision would not necessarily lead to reaction. During collisions, some of the molecules acquire large amount of energy and those molecules which would have energy greater than the activation energy are capable of undergoing transformation. It can be at least qualitatively visualised that the high energy at the moment of impact will be available to effect the necessary rearrangement of the atoms in the molecule leading to the reaction. Those collisions only which raise the molecules to the activation energy level are effective in causing chemical change.

That every collision will not lead to chemical reaction is easily seen. In the reaction



at 700°K , the number of collisions per c.c. $Z \approx 10^{28}$, whereas from kinetic measurement, the number of HI decomposed per c.c. under the same condition is of the order of 10^{18} . Hence every collision is not effective.

Again, the number of collisions (Z) per c.c. in a gas phase is given by equations 1.72 and 1.73, as

$$Z = \frac{1}{\sqrt{2}} \pi \sigma^2 C_a n^2 = \frac{1}{\sqrt{2}} \pi \sigma^2 n^2 \sqrt{\frac{8RT}{\pi M}} = B\sqrt{T} \text{ (for gases of single species),}$$

$$\text{or } Z = (\sigma_a + \sigma_b)^2 \sqrt{\frac{\pi RT}{2\mu}} n_a n_b = B'\sqrt{T} \text{ (for collision between two species)}$$

i.e., the number of collisions is proportional to $T^{\frac{1}{2}}$.

Hence,

$$Z_{710^\circ}/Z_{700^\circ} = \sqrt{\frac{710}{700}} = 1.01.$$

If every collision were effective then, for 10° degree rise in temperature, the increase in reaction rate would have been 1%. But kinetic measurements show that the reaction rate often increases by 200% or more, for 10° rise in temperature.

Let us first consider some bimolecular reactions, for which the collision theory has been found to be quite satisfactory. If the reaction be a gaseous one, such as $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$, the calculations for collision numbers etc. would be simpler, and in fact the collision theory restricts itself generally to gaseous reactions. As a result of incessant collisions, there is interchange of energy between the molecules. There would always be some molecules, governed by the distribution law, which would possess energy much larger than the average value. When molecules collide vigorously enough to reach an energy level higher than the activation energy level E_x (Fig. XV.4), the chemical change occurs. Considering the molecules as rigid spheres, the activation energy acquired may be regarded as wholly translational.

Now the proportion of activated molecules having excess energy equal to activation energy (E) or greater, at temperature T is given by the Boltzmann factor, $e^{-E/RT}$;

$$\frac{n}{n_0} = \frac{\text{no. of activated molecules}}{\text{total number of molecules}} = e^{-E/RT}$$

If Z denotes the number of collisions per c.c., the number of effective collisions in which activated molecules will be involved will be given by $Z \cdot e^{-E/RT}$. Hence, the rate of transformation per c.c. per unit time, is

$$-\frac{dn}{dt} = Z \cdot e^{-E/RT} \quad \dots \text{ (XV.35)}$$

We have seen that the temperature variation of Z is not very conspicuous. But the other factor $e^{-E/RT}$ is quite sensitive to temperature and is responsible for high increase in reaction rate with rise in temperature.

For example, suppose $E = 40000$ cal/mole, then at 500°K , $e^{-E/RT} = e^{-40} = 4.25 \times 10^{-18}$ and at 1000°K , $e^{-E/RT} = e^{-20} = 2.06 \times 10^{-9}$. Hence, reaction velocity will increase $2.06 \times 10^{-9} / 4.25 \times 10^{-18}$ or 5×10^8 times when temp. is raised by 500°C .

Also at a const. temp. the greater is E , the smaller would be the reaction velocity.

The collision number Z is obtained using molecular diameter from viscosity data. The activation energy (E) is determined from reaction-rate measurements at two temperatures. Thus the reaction rate theoretically can be calculated from equation (XV.35) and then compared with experimental value from kinetic measurements to test the theory. The results are found to be satisfactory for many gas-reactions and reactions in solution especially when the reacting molecules are simple. In reactions involving complex molecules, the observed reaction rates are markedly different from those calculated with the equation given above.

The decomposition of hydrogen iodide is a bimolecular reaction. If c be the concentration of HI at any time t , then

$$\frac{-dc}{dt} = kc^2 \quad \dots (A)$$

Now $c = \frac{n}{N} \times 10^3$, where n = no. of molecules per c.c. ; N_0 = Avo. number.

$$\therefore \frac{dc}{dt} = \frac{10^3}{N_0} \cdot \frac{dn}{dt} \quad \dots (B)$$

Substituting (B) in (A) and eliminating c ,

$$-\frac{10^3}{N_0} \frac{dn}{dt} = k \left(\frac{n}{N_0} 10^3 \right)^2$$

$$\text{or} \quad -\frac{dn}{dt} = k \left(\frac{10^3 \times n^2}{N_0} \right)$$

Comparing with equation (XV.35),

$$\text{rate constant, } k = \frac{N_0}{n^2 \times 10^3} Z e^{-E/RT} \quad \dots (XV.36)$$

For HI-molecules, the number of collisions per c.c. (Z) is

$$Z = \frac{1}{\sqrt{2}} \pi \sigma^2 n^2 \sqrt{\frac{8RT}{\pi M}}$$

Since two molecules are involved in each collision, the number of molecules colliding is $4\sigma^2 n^2 \sqrt{\frac{\pi RT}{M}}$.

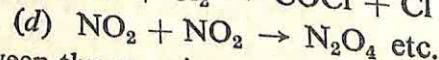
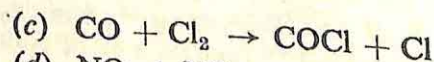
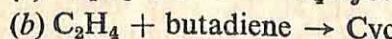
$$\begin{aligned} \text{Hence} \quad k &= \frac{N_0}{n^2 \times 10^3} \times 4\sigma^2 n^2 \sqrt{\frac{\pi RT}{M}} \cdot e^{-E/RT} \\ &= \frac{4\sigma^2 N_0}{10^3} \sqrt{\frac{\pi RT}{M}} e^{-E/RT} \quad \dots (XV.37) \end{aligned}$$

Substituting the standard values of $\sigma = 3.5 \text{ \AA}$, and $E = 44000$ cal at 556° (from Bodenstein's experiments), the value of k calculated with eqn. XV.37 for hydrogen iodide decomposition at 556°K is

$$k_{556^\circ} = 5.2 \times 10^{-7} \text{ litres/mole-sec.}$$

The experimental value is 3.5×10^{-7} . Considering the sweeping approximations used, the agreement is regarded as quite good.

In many other reactions, such as



satisfactory agreement has been found between the experimental results and those

calculated from the collision formulations. These establish not only the truth of the Arrhenius equation but also that the concept of the activation energy is basically right.

If the reaction were between two species, the expression for k would be,

$$k = (\sigma_A + \sigma_B)^2 \cdot \frac{N_0}{10^3} \cdot \sqrt{\frac{\pi RT}{2\mu}} \cdot e^{-E/RT} \quad \dots (XV.38)$$

Theoretically the velocity constant may therefore be expressed as,

$$k = A' \cdot \sqrt{T} \cdot e^{-E/RT} \quad \dots (XV.39)$$

where A' is constant for a given reaction.

The Arrhenius equation (XV.31) gives $k = A \cdot e^{-E/RT}$.

$\therefore$ The frequency factor, $A = A' \sqrt{T}$.

From equation (XV.39),

$$\ln k = \ln A' + \frac{1}{2} \ln T - \frac{E}{RT}, \quad \text{or} \quad \frac{\partial \ln k}{\partial T} = \frac{E + \frac{1}{2} RT}{RT^2} \quad \dots (XV.39a)$$

Hence a plot of $\ln k$ vs. $1/T$ will not be a straight line. The experimental observation of the linearity is due to the fact that $\frac{1}{2} \ln T$ is negligible compared to the other terms.

One question however arises in this connection. What is the nature and origin of the activation energy? The reacting molecules might acquire the energy from translational, potential, vibrational, rotational energies etc. We have, in our calculation with collision theory, used the term $e^{-E/RT}$, in which only two square terms or two degrees of freedom were utilised [eqn. I. 42]. It is tacitly assumed that the energy concerned is the translational energy along the direction of impact. The whole of the kinetic energy is not involved, but the translational component in one direction only along the line of head-on-collision. The energy is expressed in terms of the square of the velocity component in the appropriate direction. Hence for the two molecules coming into impact two degrees of freedom are involved. The proportion of molecules having attained this energy in the minimum, following Maxwell, is given by $e^{-E/RT}$. On collision, the translational energy is transformed into the vibrational to reach the initial level for dissociation of bonds. If other degrees of freedom were utilised, such as, say vibrational, the number of activated molecules would have been much higher and the calculated value would far exceed the experimental.

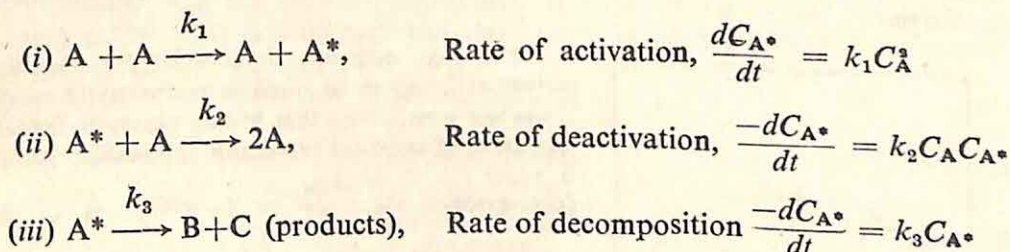
It has already been stated earlier that in some reactions the calculated values of k is higher than those experimentally found. For such reactions, the equation XV.35 is often written as

$$\text{Rate} = PZ e^{-E/RT} \quad \dots (XV.40)$$

where P is called the *steric factor* or *probability factor* and it contains the disparity between observed and calculated rate constants. The disparity is due to two reasons. For a reaction to occur as a result of a collision, acquiring the activation energy is not enough but also a suitable orientation of the colliding molecules is necessary. With larger molecules many collisions would take place where the vulnerable reactive parts would not be brought together although the molecules have high energy. In consequence many such impacts of activated molecules become infructuous, the steric factor P becomes much less than unity. Secondly, in our calculation for activation energy only the translational energy has been recognised. But there may be contribution from rotational and vibrational degrees of freedom. If such contributions be appreciable, then the observed rate of reaction would be greater than the calculated rate. It is easily seen that for these reasons correct theoretical prediction for reaction rates is difficult in case of reactions with large molecules.

XV.16. Collision Theory and Unimolecular Reactions. Although the collision theory explains the mechanism of bimolecular reactions, but with unimolecular reactions, the theory apparently fails. In the unimolecular reactions which are also of the first order, only one molecule takes part in the reaction. It is generally

accepted that in thermal reactions molecules become activated through collisions, the rate of formation of activated molecules should be proportional to the number of two-body collisions and hence should be a bimolecular process. How then the observed rate of reaction could be of the first order? In a first order reaction, the fraction of the reactant decomposing per unit time is independent of pressure or concentration. Thus, with a lowering of pressure or concentration the number of collisions will decrease but the reaction rate will remain the same. How will the molecules be activated in such circumstances? In 1919, Perrin suggested that the molecules are activated by absorption of infrared radiations. But this view was found to be unsatisfactory and finally rejected. A solution to the problem was finally offered by Lindemann (1922) which is now considered to be the most satisfactory. According to Lindemann hypothesis, the molecules acquire activation-energy through collisions, but the activated molecules decompose only after some time has elapsed after the collision. That is, there is a time-lag between the moment of activation and the moment of decomposition. When this time-lag is relatively large, there is every possibility for most of the activated molecules being deactivated through subsequent collisions to ordinary molecules. As a result, the rate of decomposition will not be proportional to all the activated molecules but only to a fraction which survives the time-lag. The activated molecules therefore disappear through two parallel processes, namely through deactivation and through decomposition. These ideas may be formulated as follows :



where A represents ordinary and A^* activated molecules.

The rate of reaction of A is the rate at which products are formed, i.e.,

$$\frac{-dC_A}{dt} = \frac{dC_B}{dt} = k_3 C_{A^*}$$

Now, activated molecules are short-lived and have a small concentration at any time during the process. So from the steady-state principle, the rate of formation of A^* molecules and the rate of their disappearance would be the same. Hence.

$$k_1 C_A^2 = k_2 C_A C_{A^*} + k_3 C_{A^*}$$

$$\text{or } C_{A^*} = \frac{k_1 C_A^2}{k_2 C_A + k_3}$$

$$\therefore \text{Rate of reaction, } \frac{-dC_A}{dt} = k_3 C_{A^*} = \frac{k_1 k_3 C_A^2}{k_2 C_A + k_3} \quad \dots \text{ (XV.41)}$$

Case (i). When rate of deactivation is very large compared with that of decomposition, i.e., when $k_2 C_A \gg k_3$, we find

$$\frac{-dC_A}{dt} = \frac{k_1 k_3}{k_2} C_A = k' C_A$$

which is the expression for the first order. This happens when time-lag is relatively large.

Case (ii). When concentration C_A is lowered considerably, the chances of deactivation by collision decreases largely, then $k_3 \gg k_2 C_A$, hence we have

$$\frac{-dC_A}{dt} = k_1 C_A^2$$

That is, at low concentration the process would follow a second order kinetics.

A behaviour of this kind as predicted by Lindemann's hypothesis has been observed in many unimolecular processes. The thermal gaseous decomposition of azomethane, and many other first order reactions, have been found experimentally to tend to the second order at very low pressures. This may be tested further. Equation (XV.41) may be written as

$$-\frac{1}{C_A} \frac{dC_A}{dt} = \frac{k_1 k_3 C_A}{k_2 C_A + k_3}$$

As before, at high concentrations, (deactivation being prominent), $k_2 C_A \gg k_3$.

Hence

$$-\frac{1}{C_A} \frac{dC_A}{dt} = \frac{k_1 k_3}{k_2} = \text{constant.}$$

But when concentration is low, $k_2 C_A \ll k_3$, $-\frac{1}{C_A} \frac{dC_A}{dt} = k_1 C_A$.

That such a condition really exists is seen from Fig. XV.5 where $-\frac{1}{P_i} \cdot \frac{dp}{dt}$ vs P_i (initial pressure) is plotted for the decomposition of azomethane (Ramsperger, 1927). As expected at high pressures (P_i), the curve is horizontal with the pressure axis, and at low pressures it increases proportionally with P_i . The unimolecular reactions are thus explained by collision mechanism on the basis of Lindemann hypothesis.

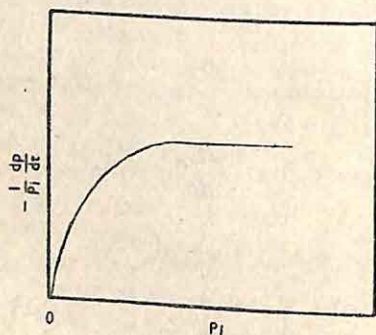


FIG. XV.5 Plot of $-\frac{1}{P_i} \frac{dp}{dt}$ vs P_i

for decomposition of azomethane

10^6 times higher than the rate of formation of activated molecules calculated from simple collision theory.

It may be remembered that in formulating the collision theory we assumed, for acquiring activation energy, only two translational degrees of freedom. It is now believed that in unimolecular processes (where E is usually large), the activation energy is acquired not only from the translational but also from other degrees of freedom, such as vibrational, rotational, etc. In other words, a number of degrees of freedom (S) are utilised in supplying the activation energy. A classical computation of molecules having energy greater than E , acquired from S degrees of freedom is given by

$$\frac{(E/RT)^{\frac{1}{2}S-1} \cdot e^{-E/RT}}{(\frac{1}{2}S-1)!}$$

Hence, rate of formation of activated molecules = $z \cdot \frac{(E/RT)^{\frac{1}{2}S-1}}{(\frac{1}{2}S-1)!} e^{-E/RT}$

The pre-exponential factor is thus altered. And,

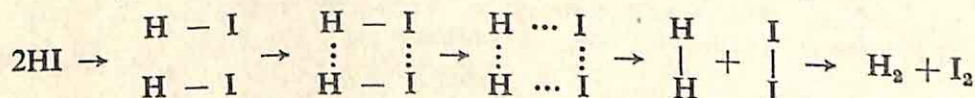
$$\frac{d \ln k}{dT} = \frac{E - (\frac{1}{2}S-1)RT}{RT^2}$$

Suitable values of S give results in conformity with the experimental values. Thus, in unimolecular reaction, the Arrhenius equation for the variation of velocity constant with temperature is also modified.

XV.17. The Transition-State Theory. Another approach, as an alternative to the collision theory, to explain the mechanism of reactions has been made. This approach, known as the *transition-state theory* or the *absolute reaction-rate theory* was first outlined by Marcellin (1915) and was put in its developed present form in 1935 by Eyring and by Polanyi. According to this theory, the reactant molecules are first transformed into an intermediate energy-rich *activated complex* or *transition state*. This activated complex may be formed by some loose association or bonding of the reactant molecules with necessary rearrangement of valence bonds and energy. Or if it be a unimolecular reaction, the reactant molecule may produce the activated complex by rearrangement of atoms and redistribution of energy. In any case, the activated complex, though unstable and has a transient existence, is treated formally as a definite molecule with an independent entity. The activated complex subsequently breaks up to produce the resultants at a definite rate.

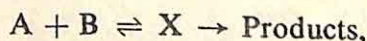
Schematically, $\text{Reactants} \rightleftharpoons \text{Activated complex} \rightarrow \text{Products}$.

In considering the HI-dissociation, we may visualise it as follows :



As to the activated complex, the following postulates are accepted.

(a) The activated complex is regarded as a separate entity, and it is always in equilibrium with the reactant molecules. If C_A and C_B be the concentration of reactants and $C^\ddagger$ is the concentration of the activated complex (X) in the reaction,



$$\text{the eqm. const.,} \quad K^\ddagger = \frac{C^\ddagger}{C_A \cdot C_B} \quad \dots \text{(XV.42)}$$

$$\text{or} \quad C^\ddagger = K^\ddagger \cdot C_A \cdot C_B \quad \dots \text{(XV.43)}$$

The suffix ($\ddagger$) refers to the activated complex.

(b) The activation energy (E) of the reaction is the additional energy which the reactant molecules acquire to form the activated complex (X). The energy of the activated complex will thus be sufficient to reach the peak of the curve in Fig. XV.4.

(c) The activated complex must have one of its vibrational degrees of freedom which would be quite unstable. This vibration is responsible for disrupting the complex into the products. The vibration happens to have a large enough amplitude to break open the complex. The frequency of such vibrations will be low and the average energy will be of the order of kT . If ν be the frequency of this vibration, then

$$h\nu = \epsilon_{vib} = kT \quad (h = \text{Planck's constant})$$

$$\text{or} \quad \nu = kT/h \quad (k = \text{Boltzmann constant})$$

Those of the activated complex attaining this frequency of vibration per sec. shall undergo decomposition. In other words, this frequency is something similar to the rate at which the complex will break up into reaction products. Hence,

$$\text{rate} = \nu \cdot C^\ddagger \text{ (molecules/c.c.-sec.)} \quad \text{(XV.44)}$$

Substituting from eqn. XV.43 ; $\text{rate} = \nu \cdot K^\ddagger \cdot C_A \cdot C_B$.

If k_1 be the velocity constant of the reaction, then $\text{rate} = k_1 C_A \cdot C_B$. Comparing these two, we have ,

$$k_1 = \nu \cdot K^\ddagger = \frac{kT}{h} \cdot K^\ddagger \quad \dots \text{(XV.45)}$$

$$\text{or} \quad k_1 = \frac{RT}{Nh} K^\ddagger \quad \dots \text{(XV.45a)}$$

This expression is valid not only for two reactants ; it is true for any reaction.

The equilibrium constant $K^\ddagger$ can be expressed either in terms of molecular partition functions or in terms of thermodynamic quantities. We shall follow here the thermodynamic approach. The equilibrium constant K of a process is related to the thermodynamic potential change (ΔG) by the relation, $RT \ln K = -\Delta G^\circ$. i.e.,

$$K = e^{-\Delta G^\circ/RT}$$

For the formation of the activated complex, therefore, $K^\ddagger = e^{-\Delta G^\circ/RT}$

$$\text{or} \quad \text{rate constant, } k_1 = \frac{RT}{Nh} e^{-\Delta G^\circ/RT} \quad \dots \text{ (XV.45b)}$$

According to this theory the activated complex is the state of maximum thermodynamic potential in the course of the reaction. Evidently, the specific rate of a reaction is determined by $\Delta G^\ddagger$, the thermodynamic potential of activation. The higher the value of $\Delta G^\ddagger$, the slower is the reaction rate at a given temperature. This emphasizes the thermodynamic potential change of activation as the fundamental quantity rather than the energy of activation. Again, the thermodynamic potential change of activation may be expressed as,

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

where $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are the standard enthalpy and entropy of activation.

[The suffix $^\circ$ is dropped for convenience of writing.]

$$\therefore \quad \text{Eqm. constant, } K^\ddagger = e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad \dots \text{ (XV.45c)}$$

In other words, the rate constant (k_1) is given by

$$k_1 = \frac{RT}{Nh} \cdot e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad \dots \text{ (XV.46)}$$

The difference between $\Delta H^\ddagger$, enthalpy of activation and E , energy of activation (Arrhenius) is indeed small. In fact, for reactions in solution, the two quantities are equal. For gaseous reactions a correction ΔnRT has to be introduced. Thus, without much error, it may be written as

$$k_1 = \frac{RT}{Nh} e^{\Delta S^\ddagger/R} e^{-E/RT} \quad \dots \text{ (XV.47)}$$

On comparing this with the Arrhenius equation (XV.31), $k_1 = A \cdot e^{-E/RT}$, the frequency factor (A) would be,

$$A = \frac{RT}{Nh} e^{\Delta S^\ddagger/R} \quad \dots \text{ (XV.48)}$$

*From eqn. XV.45a.,

$$\frac{d \ln k_1}{dT} = \frac{1}{T} + \frac{d \ln K^\ddagger}{dT}$$

But from eqn. XV.29 :

$$\frac{d \ln k_1}{dT} = \frac{E}{RT^2}$$

$$\text{Hence, } E = RT + RT^2 \frac{d \ln K^\ddagger}{dT} = RT + \Delta E^\ddagger = RT + \Delta H^\ddagger - \Delta nRT$$

$$\text{i.e., } -\Delta H^\ddagger = -E - RT(\Delta n - 1), \text{ or } e^{-\Delta H^\ddagger/RT} = e^{-E/RT} \cdot e^{-(\Delta n - 1)}$$

where Δn = increase in number of molecules when activated complex is formed. So the more

accurate expression for k_1 is

$$k_1 = e^{-(\Delta n - 1)} \frac{RT}{Nh} e^{\Delta S^\ddagger/R} e^{-E/RT}$$

For unimolecular process, $\Delta n = 0$, hence $k_1 = e \cdot \frac{RT}{Nh} e^{\Delta S^\ddagger/R} e^{-E/RT}$.

For bimolecular process $\Delta n = -1$, hence $k_1 = e^2 \cdot \frac{RT}{Nh} e^{\Delta S^\ddagger/R} e^{-E/RT}$

In our discussions here, the factor e or e^2 is ignored.

It must be remembered that in the collision theory, the frequency factor A is equal to the collision frequency (Z) or proportional to Z (eqn. XV.40). In transition state theory A has a different meaning, it is a measure of the entropy of activation. On taking logarithms, equation XV.47 takes the form

$$\ln k_1 = \left\{ \Delta S^\ddagger/R + \ln \frac{R}{Nh} \right\} + \ln T - \frac{E}{RT} \quad \dots \text{(XV.47a)}$$

Since $\Delta S^\ddagger$ is practically independent of temperature and $\ln T$ is negligible in comparison to E/RT , a plot of $\log k_1$ against $1/T$ would be linear. This has already been experimentally established by Arrhenius. [Compare also eqn. XV.39a].

For gaseous reactions, the entropy of activation is *generally* negative. This may be qualitatively explained as follows. When two reactant molecules come to produce the activated complex, the total translational degrees of freedom are reduced (from 6 to 3) and the rotational degrees of freedom also diminish. This is compensated by increase in vibrational degrees of freedom. But the definite orientation in forming the complex necessarily reduced the entropy. The value of $\Delta S^\ddagger$ is thus negative. When the reactant molecules are simple, the decrease in entropy in complex formation is small. But when large polyatomic molecules are involved there would be a large decrease in entropy. Larger the decrease in entropy, smaller will be the value of A . In a few simple reactions, the value of A calculated from eqn. XV.48 corresponds to the collision frequency Z . But with polyatomic reactants the value of A is found to be considerably smaller due to a large decrease in entropy. The smaller magnitude of A (lower than collision frequency Z) has been explained in collision theory by introducing steric factor P for infructuous collisions (eqn. XV.40) and by large entropy-drop in transition state theory.

$$\text{Since } \frac{R}{Nh} = \frac{8.3 \times 10^7}{6 \times 10^{23} \times 6.6 \times 10^{-27}} \approx 2 \times 10^{10},$$

$$\text{the velocity constant, } k_1 = 2 \times 10^{10} T e^{\Delta S^\ddagger/R} e^{-E/RT}$$

For bimolecular gaseous reactions, it is estimated that the entropy of activation ranges between -10 cal/mole/degree and -40 cal/mole/degree. That is, the velocity constant would have the limits,

$$k_1 = 2 \times 10^{10} T e^{-5} e^{-E/RT} \quad \text{and} \quad k_1 = 2 \times 10^{10} T e^{-20} e^{-E/RT}$$

$$\text{i.e., it will lie between } k_1 = 10^8 T e^{-E/RT} \text{ and } k_1 = 10^2 T e^{-E/RT}$$

In many unimolecular processes, the entropy changes very little in the formation of the activated complex, i.e., $\Delta S^\ddagger$ is very small and may even be positive.

$$\text{Hence, } k_1 = 2 \times 10^{10} T e^{-E/RT}.$$

Illustrations : (a) In the bimolecular decomposition of HI, the activation energy is $E = 44300$ cal. Assuming $\Delta S^\ddagger = -10$ cal/degree, we have the rate constant, at 556°K ,

$$k = 10^8 T e^{-E/RT} = 10^8 \times 556 \times e^{-44300/2 \times 556} = 2.8 \times 10^{-7} \text{ litres/mole-sec.}$$

The experimental value is 3.5×10^{-7} . Compare this with the result obtained from collision theory formulation (eqn. XV.37).

(b) The conversion of cyclopropane into propylene is a unimolecular process with the energy of activation, $E = 65000$ cal, at 500°C .

$$\text{The rate constant } k = e \frac{RT}{Nh} e^{\Delta S^\ddagger/R} e^{-E/RT}$$

(The factor e is taken for correction in changing $\Delta H^\ddagger$ to E , vide foot note page 654). Putting standard values, $k = 4.4 \times 10^{13} e^{\Delta S^\ddagger/R} e^{-65000/2 \times 773}$

Experimentally by plotting $\log_{10} k$ against $\frac{1}{T}$ it was found to follow the relation

$$\log_{10} k = 15.17 - \frac{65000}{2.3 RT}$$

$$\text{i.e., } k = 1.48 \times 10^{16} e^{-65000/RT}$$

Equating the frequency factor, $4.4 \times 10^{13} e^{\Delta S^\ddagger/R} = 1.48 \times 10^{15}$

whence $\Delta S^\ddagger \approx 7$ calories/degree/mole.

For reactions in solution the solvation effect is involved. When two solvated reactant molecules form an activated complex, the definitely oriented solvent molecules adhering to the reactants move away and the restriction on motion of the solvent molecules is relaxed. There is thus an increase in solvation entropy. In consequence, the net entropy may increase even if real entropy of activation is negative. As such in many reactions in solution $\Delta S^\ddagger$ is found to be positive.

Reaction	$\Delta S^\ddagger$
(a) $\text{Fe}^{+++} + \text{CNS}^- = \text{Fe}(\text{CNS})^{++}$	14.0
(b) $\text{CH}_2(\text{COOH})\text{COO}^- = \text{CH}_2(\text{COO})_2^{--} + \text{H}^+$	-29.9

XV.18. Chain Reactions. The reactions which have so far been considered are explained in terms of mechanism of their taking place either in a single step or in a series of intermediate steps. The intermediate steps ultimately lead to the products. There is however a group of reactions which proceed by a long series of self-repeating steps. When the final product is formed, the active intermediate species is regenerated to carry on the reaction. Such reactions are called *chain reactions*.

In 1906 Bodenstein found that the reaction between H_2 and Br_2 was not a simple bimolecular one like that between H_2 and I_2 . The reaction was a complicated one and appeared to follow a kinetics expressed by the relation,

$$\frac{dC_{\text{HBr}}}{dt} = \frac{k C_{\text{H}_2} \cdot C_{\text{Br}_2}^{\frac{1}{2}}}{1 + k' C_{\text{HBr}}/C_{\text{Br}_2}} \quad \dots (\text{XV.50})$$

Since C_{HBr} is in the denominator, it is likely to inhibit the process.

No explanation of such results was available until in 1920 Christiansen, Herzfeld and Polanyi all independently proposed a scheme of self-propagating steps in the formation of HBr . At the first stage, molecules of bromine are dissociated into atoms. The Br-atoms then carry on the process in the following way :

		rate constants
Chain initiation	(1) $\text{Br}_2 \rightarrow 2\text{Br}$	k_1
Chain propagation	(2) $\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$	k_2
	(3) $\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}$	k_3
Chain inhibition	(4) $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$	k_4
Chain-break	(5) $\text{Br} + \text{Br} \rightarrow \text{Br}_2$	k_5

Evidently the process is initiated with formation of Br-atoms in (1). A Br-atom then leads to the formation of HBr through reactions (2) and (3). Two molecules of HBr are formed and the Br-atom is regenerated to continue the cycle. These self-propagating steps are likely to continue endlessly through repeated generation of chains of Br-atoms and H-atoms. Thus for any initial Br-atom, a large number of HBr would result. Only sometimes a chance collision between a H and HBr (4) inhibits the process or when two Br-atoms come together to unite into a Br_2 -molecule, the chain is broken or stopped. In fact in all chain reactions, three stages are involved : (i) the initiation of the chain (ii) the propagation of the chain and (iii) the breaking of the chain.

We can proceed to derive the kinetic law of the process on the basis of the scheme presented. Br-atoms and H-atoms are the active short-lived intermediates and must have low concentrations. The steady state concept can be applied in these, So, we have,

$$(A) \quad \frac{dC_{\text{Br}}}{dt} = k_1 C_{\text{Br}_2} - k_2 C_{\text{Br}} C_{\text{H}_2} + k_3 C_{\text{H}} C_{\text{Br}_2} + k_4 C_{\text{H}} C_{\text{HBr}} - k_5 C_{\text{Br}}^2 = 0$$

$$(B) \quad \frac{dC_{\text{H}}}{dt} = k_2 C_{\text{Br}} C_{\text{H}_2} - k_3 C_{\text{H}} C_{\text{Br}_2} - k_4 C_{\text{H}} C_{\text{HBr}} = 0$$

$$\text{Adding (A) and (B),} \quad k_1 C_{\text{Br}_2} - k_5 C_{\text{Br}}^2 = 0$$

$$(C) \text{ or, } C_{\text{Br}} = \sqrt{\frac{k_1}{k_5} C_{\text{Br}_2}} = k_6 C_{\text{Br}_2}^{\frac{1}{2}}, \quad \text{where } k_6 = \left(\frac{k_1}{k_5} \right)^{\frac{1}{2}}$$

We also have from (B),

$$C_H = \frac{k_2 C_{Br} C_{H_2}}{k_3 C_{Br_2} + k_4 C_{HBr}}$$

(D) or
$$C_H = \frac{k_6 k_2 C_{H_2} C_{Br_2}^{\frac{1}{2}}}{k_3 C_{Br_2} + k_4 C_{HBr}}, \text{ substituting from (C)}$$

Now, hydrobromic acid is formed by reactions (2) and (3) and disappears by reaction (4). So, the rate of its formation is

(E)
$$\frac{dC_{HBr}}{dt} = k_2 C_{Br} C_{H_2} + k_3 C_H C_{Br_2} - k_4 C_H C_{HBr}$$

From (B) we know, $k_2 C_{Br} C_{H_2} - k_4 C_H C_{HBr} = k_3 C_H C_{Br_2}$.

Substituting this in (E),

$$\begin{aligned} \frac{dC_{HBr}}{dt} &= 2k_3 C_H C_{Br_2} \\ &= \frac{2k_3 k_6 k_2 C_{H_2} C_{Br_2}^{\frac{1}{2}} C_{Br_2}}{k_3 C_{Br_2} + k_4 C_{HBr}} \quad [\text{substituting (D)}] \end{aligned}$$

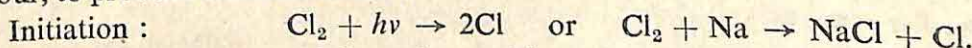
Dividing both numerator and denominator by $k_3 C_{Br_2}$,

$$\frac{dC_{HBr}}{dt} = \frac{2k_6 k_2 C_{H_2} C_{Br_2}^{\frac{1}{2}}}{1 + \frac{k_4 C_{HBr}}{k_3 C_{Br_2}}}$$

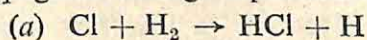
or
$$\frac{dC_{HBr}}{dt} = \frac{k C_{H_2} C_{Br_2}^{\frac{1}{2}}}{1 + k' C_{HBr}/C_{Br_2}} \quad \dots (XV.51)$$

($k = 2k_6 k_2$, $k' = k_4/k_3$). It is the same relation found by Bodenstein (XV.50). All the constants k_1, k_2 etc. have been evaluated.

The reaction of hydrogen and chlorine to give hydrogen chloride is also a chain-process propagated through H- and Cl-atoms. The chain is first initiated, by momentary exposure of the system to light or introduction of a trace of sodium-vapour, to produce chlorine atoms :

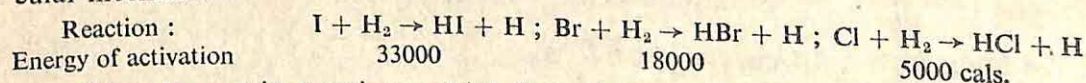


Then the chain is propagated through repetition of

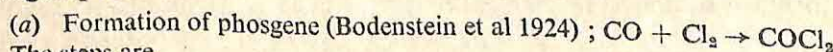


The reaction rate is often greatly influenced by traces of moisture and oxygen and by glass-surfaces of the container. Free from these interferences, about 10^6 molecules of HCl are formed for each initiating chlorine atom.

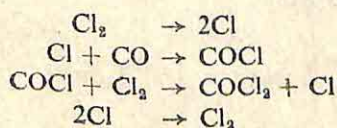
In answer to the question as to why H_2-I_2 reaction does not follow a chain mechanism, it is revealed that the energy of activation in the process $I + H_2 \rightarrow HI + H$, is relatively high ($E = 33$ K cal) and hence it follows the easier path of bimolecular mechanism.



Other inorganic reactions which have been established to proceed through chain propagation include the formation of phosgene and the decomposition of nitrogen pentoxide:

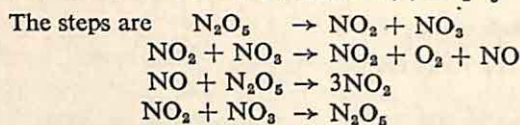


The steps are



$$\frac{dC_{COCl_2}}{dt} = k C_{CO} C_{Cl_2}^{\frac{1}{2}}$$

(b) Decomposition of N_2O_5 (Ogg, 1947) ; $2N_2O_5 \rightarrow 4NO_2 + O_2$



When

$$\frac{-dC_{N_2O_5}}{dt} = kC_{N_2O_5}$$

Soon many other reactions, specially organic ones, were found in which the chains propagated through radicals.

XV.19. Free-Radical Chains. The existence of free methyl radicals was first established by Paneth and Hofeditz in 1929 from the dissociation of lead tetramethyl. The readily volatile lead tetramethyl liquid was taken in an evacuated container (Fig. XV.6). A stream of H_2 -gas at low pressure carried the vapour of lead tetra-

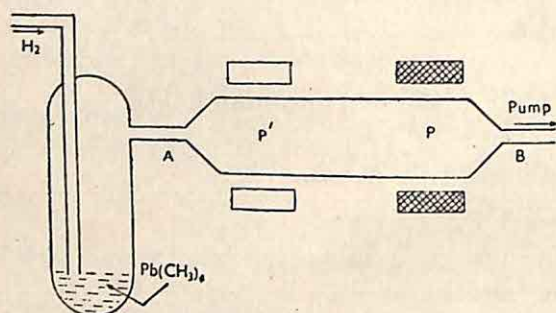


FIG. XV.6 Detection of free methyl radicals

methyl into the tube AB. The gases are taken out by a high speed vacuum pump at the end B. A small furnace surrounds the tube AB at the point P, where a lead mirror is deposited from the decomposition of $Pb(CH_3)_4$. Next the furnace is moved up to the point P'. A new mirror is deposited at P' and the mirror at P now slowly disappears. Obviously, the CH_3 -radicals set free at P' are carried with the gas-stream downwards and attack the mirror at P forming again $Pb(CH_3)_4$.

Rice and co-workers developed the technique and succeeded in producing and dealing with different radicals. In the thirties of the century, Rice, Herzfeld and others explained the kinetic laws governing many organic reactions on the basis of chain propagation through radicals. As an illustration we may take the thermal decomposition of acetaldehyde.

The chain mechanism is initiated by the formation of a methyl radical which follows the steps as :

		Rate constant
Chain initiation	(i) $CH_3CHO \rightarrow CH_3 + CHO$	k_1
Chain propagation	(ii) $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$	k_2
	(iii) $CH_3CO \rightarrow CO + CH_3$	k_3
Chain breaking	(iv) $CH_3 + CH_3 \rightarrow C_2H_6$	k_4

The steady-state concept may be applied to the short-lived intermediates, CH_3 and CH_3CO radicals ; their concentrations remain constant. Hence,

$$\frac{dC_{CH_3}}{dt} = k_1C_{CH_3CHO} - k_2C_{CH_3CHO} \cdot C_{CH_3} + k_3C_{CH_3CO} - k_4C_{CH_3}^2 = 0$$

$$\text{and } \frac{dC_{CH_3CO}}{dt} = k_2C_{CH_3CHO} \cdot C_{CH_3} - k_3C_{CH_3CO} = 0$$

$$\text{Adding these, } k_1C_{CH_3CHO} = k_4C_{CH_3}^2$$

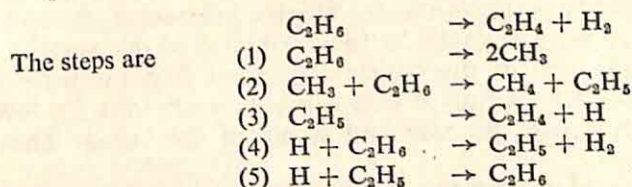
$$\text{or } C_{CH_3} = \left(\frac{k_1}{k_4} \cdot C_{CH_3CHO} \right)^{\frac{1}{2}}$$

The rate of formation of methane, i.e., the rate of decomposition of the aldehyde is

$$\begin{aligned} \frac{dC_{CH_4}}{dt} &= k_2C_{CH_3} \cdot C_{CH_3CHO} \\ &= k_2 \left(\frac{k_1}{k_4} \right)^{\frac{1}{2}} C_{CH_3CHO}^{\frac{3}{2}} = kC_{CH_3CHO}^{\frac{3}{2}} \end{aligned}$$

The decomposition thus follows the three-halves kinetic order.

Similar radical chain mechanism explains many other reactions, such as the decomposition of ethane, (Pease, 1928).



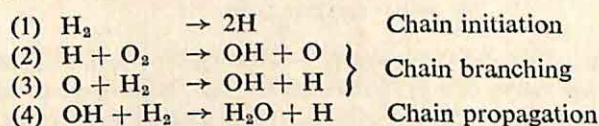
By the usual steady-state treatment, it can be shown

$$\frac{dC_{C_2H_5}}{dt} = k C_{C_2H_6}$$

XV.20. Branching Chain. Explosions. In the chain reactions considered thus far, it is seen that when one free radical (or atom) disappears another is produced in its place along with the product and the chain is carried on. These atoms or free radicals are the chain carriers. With the steady state concept, the concentration of the chain carrier is regarded as finite and small.

In some gas-phase oxidation reactions such as the oxidation of hydrogen, carbon monoxide, phosphine, carbon-disulphide etc. which proceed through a chain-mechanism, each chain carrier produces more than one free-radical. The result is that the concentration of the active species of chain-carrier will increase rapidly with time with a consequent rapid increase in the reaction rate. This in turn would further increase the production of free radicals. The reaction then occurs instantaneously and an explosion takes place. The chain is said to *branch* when an active species or chain carrier would produce more than one free radical or carrier.

The hydrogen-oxygen reaction is now believed to follow the mechanism :



In the elementary processes (2) and (3), we find that from each atom of hydrogen, two radicals are produced which propagate the chain. Hence a branching of chain occurs. When the reaction proceeds to some extent, the amounts of free-radicals would be very large and an explosive reaction would occur. The free radicals or chain carriers may also be destroyed, mainly by collision with the walls.

In these reactions there are some striking features. Below a certain pressure, the reaction proceeds slowly and smoothly. Immediately above this pressure, the reaction rate jumps to an explosion. As the pressure is further increased, explosion continues until a second pressure limit called the upper limit is reached, above which the explosion ceases and a steady reaction follows. With further rise in pressures the reaction rate increases and a third limit is reached leading again to explosion. These limits are schematically shown in Fig. XV.7.

The explanation is simple. At low pressures, the radicals reach the surface easily and are destroyed there. This rate of destruction counterbalances the increase of production of radicals from branching of the chain. The reaction therefore goes smoothly.

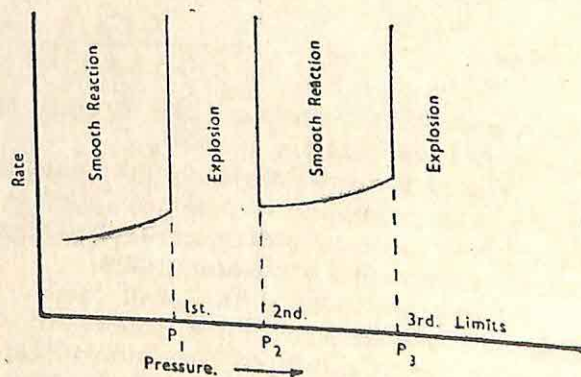
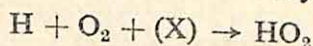


FIG. XV.7 Explosion limits

With increase in pressure, the propagation and the branching rates increase. But at higher pressure the rate of diffusion of the radicals to the walls diminish and hence rate of destruction of radicals slows down. When a pressure P_1 is reached the rate of branching is quite rapid compared to the slow rate of destruction of radicals. There is a considerable rise in the concentration of free radicals, the rate of reaction increases enormously leading to explosion. It is obvious the lower explosion limit (P_1) shall depend upon the size and shape of the vessel. This is experimentally established.

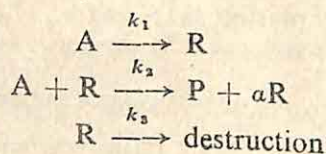
At still higher pressures (P_2 and above), the radicals are more readily destroyed internally in the gas than at the walls. The three body-collisions of the type,



(where X is a foreign gas or H_2 or O_2 molecule) would remove the carrier producing HO_2 , which does not propagate the chain. The result is, the radicals are effectively removed. The increased rate of production of radicals due to branching is thus counterbalanced, the reaction therefore proceeds smoothly.

The third limit is often due to thermal explosion. In these exothermic reactions carried out in a closed space, the heat generated often cannot be dissipated. The temperature therefore rises which also increases reaction-rate and more heat in turn is produced. The reaction rate suddenly becomes very rapid and thermal explosion takes place.

The kinetics of a reaction involving branched chain may be considered in the following way. Suppose R is the active species produced from the reactant A. If α be the number of chain carriers formed from each initial R, then the scheme of reaction may be represented as,



where P is the resultant. The k -terms are the velocity constants. The chain carriers may be destroyed in two ways either diffusing to the walls to combine in a surface reaction or by internal three-body collisions in the gas-phase. That is, k_3 is really the sum of two reaction-rate constants, k_g for gas-phase destruction and k_w for wall-destruction.

In order to have a smooth reaction, the steady state condition should prevail, that is $\frac{dC_R}{dt}$ should be zero. Hence

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_A \cdot C_R + \alpha k_2 C_A C_R - k_3 C_R = 0$$

$$\text{or} \quad C_R = \frac{k_1 C_A}{k_3 + k_2 C_A (1 - \alpha)}$$

$$\text{or} \quad C_R = \frac{k_1 C_A}{k_w + k_g + k_2 C_A (1 - \alpha)} \quad \dots (XV.52)$$

Generally in reactions, like those of $H_2 - Br_2$ or decomposition of aldehyde etc. $\alpha = 1$. So that $C_R = k_1 C_A$

When α is more than unity, branching of the chain is involved. If it so happens that α is large enough to make $k_2 C_A (\alpha - 1) = k_w + k_g$, C_R tends to infinity. The enormously large concentration of chain carriers is responsible for extremely rapid rate of reaction and explosion occurs.

At low pressures, diffusion of carriers to the wall is rapid and hence k_w is large. So long as $k_w + k_g$ is greater than $k_2 C_A (\alpha - 1)$, i.e., rate of destruction is greater than the rate of formation of carriers, smooth reaction would prevail. Then a limit of pressure is reached when fewer carriers reach the wall, k_w falls and $k_2 C_A (\alpha - 1)$ becomes relatively large and finally explosion occurs. On the

other hand, if the pressure is raised gradually, k_w will fall but k_g will increase. And when destructive collisions in the gas-phase outweigh the branching of chain, C_R diminishes and the reaction rate becomes lower. This is how the next pressure limit is reached.

CATALYSIS

XV.21. "Catalysis". It is often seen that the velocity of a reaction is altered by the presence of a foreign substance which remains unchanged at the end of the reaction. Such substances are termed "*Catalysts*". A catalyst is therefore defined as a substance that influences the speed of a chemical reaction itself remaining unchanged. The phenomenon is called catalysis. When the speed of the reaction is enhanced it is termed *positive* catalysis and if the speed is slowed down it is a case of *negative* catalysis. Thus, sulphuric acid is a positive catalyst in the hydrolysis of ester but it acts as a negative catalyst in the decomposition of hydrogen peroxide.

There are some characteristic features of the catalysed reactions. (i) *The catalyst remains unchanged in mass and in chemical composition at the end of reaction.* But its physical form may be modified profoundly. Thus, when coarsely broken manganese dioxide is used to catalyse the decomposition of potassium chlorate, the pieces are disintegrated to a very fine powder at the end of the action.

(ii) *A very minute quantity of a catalyst can produce an appreciable effect on the speed of a reaction.* For example : Titoff found that copper sulphate at a concentration of 10^{-12} gm-moles/litre would cause an appreciable increase in the rate of oxidation of sodium bisulphite by air. Bredig observed that 1.7×10^{-4} gms of platinum in colloidal suspension would liberate 1.8 c.c. oxygen per minute from hydrogen peroxide and even after 10 litres of gas being produced the activity of platinum remained as before.

(iii) *A catalyst cannot start a reaction but only increases or decreases its speed.* The possibility of a reaction is determined from the criterion whether the process would involve free-energy decrease. But the free energy decrease would not indicate if the reaction would be slow or fast. Generally speaking, if the energy of activation is large, the reaction would be quite slow. Sometimes the reaction is so slow that it is almost undetectable, but all the same the reaction is taking place. The catalyst functions as an agent to find out an alternative path which would require smaller activation energy. Usually the catalyst combines or associates with the reactant and the process is carried out in stages ultimately producing the reactants and the catalyst back. The catalyst gives rise to such steps in the process, that even in the slowest of the steps, the activation energy is less than that in the uncatalysed process.

(iv) *The catalyst does not affect the final state of equilibrium.* This indeed is a thermodynamic requirement. We know that the free-energy change (ΔF) is a perfect differential and is thus independent of the path of transformation. Since the catalyst is reproduced at the end, it does not contribute any energy to the system. The free energy change thus shall be the same whether a catalyst is present or not. Since, under standard states,

$$-\Delta F = RT \ln K$$

the equilibrium constant will be unaffected by the presence of a catalyst.

As the final position of the equilibrium is unchanged and the equilibrium constant $K = k_1/k_2$, the ratio of the velocity constants of the forward and backward reactions would remain constant. Hence the catalyst shall influence the rates of forward and reverse reactions to the same extent. Thus H^+ ion which accelerates the hydrolysis of an ester is also an accelerator for the esterification of the organic acid.

In establishing this criterion of a catalysed reaction, the equilibrium constant should be evaluated in terms of activities. If measured in terms of concentrations, the equilibrium may in some cases appear to vary. This is due to the alteration of the activity of the components in presence of catalysts.

It is convenient to divide the catalysed reactions into two groups, namely, homogeneous and heterogeneous. In homogeneous catalysis, the catalyst forms a single phase with the reactants, such as nitric-oxide in oxidation of SO_2 in the chamber process, or acids catalysing the hydrolysis of esters. In heterogeneous catalysis, the catalyst and the reactants constitute separate phases and often the surface or interface is responsible for the catalytic effect.

XV.22. Homogeneous Catalysis. Many homogeneously catalysed reactions have been studied in the gas-phase and in liquid-phase. Common examples of such catalysis in gas-phase are the catalytic effect of nitric oxide in the oxidation of carbon monoxide to dioxide or the decomposition of nitrous oxide to nitrogen and oxygen, iodine vapour catalysing the decomposition of ethers or acetaldehyde vapours, etc. The reaction rates in homogeneously catalysed reactions are invariably found to be proportional to the concentration of the catalyst.

The uncatalysed decomposition of ethyl ether is found to be a unimolecular reaction with an activation energy of 53000 cal. But when it is catalysed with iodine vapour, the reaction is a bimolecular one with the lesser activation energy of 34300 cal. The reaction rate is represented as

$$\frac{dx}{dt} = k.C_{\text{ether}}C_{I_2}$$

The fact is that the catalyst forms an intermediate compound with the reactant first and subsequently the intermediate compound breaks up or reacts to yield the products along with the original catalyst. The reactant with which the catalyst combines is often mentioned as "*substrate*". The catalyst in this way provides, with lesser energy of activation, an alternative path for the reaction in which the rate is necessarily dependent on the catalyst-concentration. Thus



where S is substrate, P products, C catalyst and X, the intermediate compound.

The rate of formation of the product, $\frac{dC_p}{dt} = k_3 C_x$

For the intermediate X, if we invoke the steady-state postulate,

$$\frac{dC_x}{dt} = k_1 C_s C_c - k_2 C_x - k_3 C_x = 0$$

$$\text{i.e.,} \quad C_x = \frac{k_1 C_s C_c}{k_2 + k_3}$$

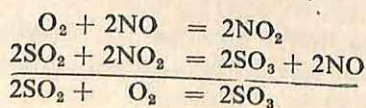
$$\text{The reaction rate,} \quad \frac{dC_p}{dt} = \frac{k_3 \cdot k_1 C_s \cdot C_c}{k_2 + k_3} = k_c C_s C_c$$

It clearly shows that the rate is dependent on catalyst-concentration (C_c). For a given concentration of the catalyst,

$$\frac{dC_p}{dt} = k' C_s$$

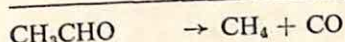
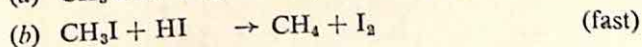
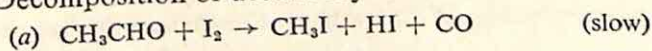
where $k' = k_c C_c$, i.e., k' is proportional to C_c . The constant k_c is known as the catalytic coefficient for the catalyst. To illustrate,

(i) Oxidation of SO_2 catalysed with NO ,



the existence of NO_2 being experimentally confirmed.

(ii) Decomposition of acetaldehyde with iodine as catalyst.



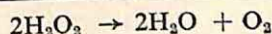
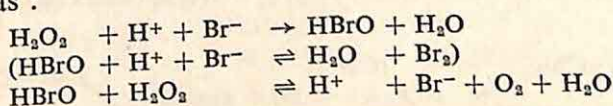
The presence of iodine enhances the speed several thousand times. The reaction rate is governed by the relatively slower stage (a), when the activation energy is 32000 cal, where as the activation energy of uncatalysed process is 45500 cal.

$$\text{The rate, } \frac{dx}{dt} = k_c \cdot C_{\text{I}_2} \cdot C_{\text{aldehyde}} = k \cdot C_{\text{aldehyde}}$$

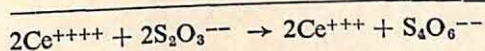
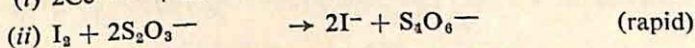
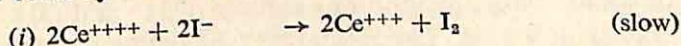
where k_c is the catalytic coefficient for the catalyst iodine for the said reaction.

Homogeneous catalysis in solution : The study of various catalysed reactions in solution have also revealed that intermediate compounds are formed between the catalyst and reactant. Some instances are cited here.

Hydrobromic acid acts catalytically in the decomposition of hydrogen peroxide. It is most likely that the reaction proceeds through the intermediate formation of HBrO as :



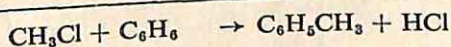
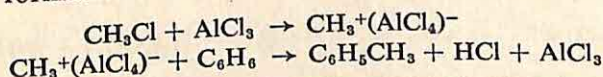
The reaction between ceric and thiosulphate ions is catalysed by iodide ions. The iodide ion is first acted by ceric ions producing iodine atom. The latter is then transformed back by thiosulphate into iodide ion.



The reaction rate depends upon the slow process (i) and hence on the concentration of the iodide ion.

Other such examples are the oxidation by persulphates with Ag^+ as catalyst, or the reaction between ceric salts and arsenites where iodide ion behaves as catalyst.

The Friedel-Crafts reaction provides also another instance of intermediate compound formation. The whole reaction is supposed to occur as

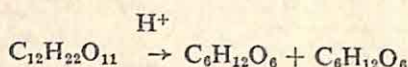


This scheme is supported from the fact that if anhydrous AlCl_3 with isotopic radio-chlorine is used, the liberated HCl shows the same activity, showing interchange of chlorine atoms of AlCl_3 and CH_3Cl . The conductance measurement of the solution also indicates the formation of the ionic addition compound $\text{CH}_3^+(\text{AlCl}_4)^-$.

But the most important homogeneously catalysed reactions are those which are classed as *acid-base catalysis*. In many liquid phase reactions, either H^+ -ion or OH^- -ion or other acids and bases individually or jointly take part in catalytic activity.

XV.23. Acid-Base Catalysis. Since early days of study it was known that inversion of cane sugar solution as also the hydrolysis of ester are catalysed by acids. Ostwald showed that different acids have different catalytic activity, hydrochloric acid has a much greater activity than that of acetic acid. When Arrhenius theory of electrolytic dissociation was established, it was evident that the real catalysts are the

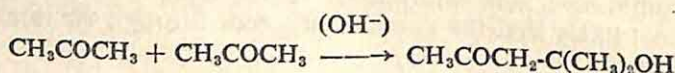
H^+ ions in the reactions mentioned above. The rates of reaction were found to be proportional to the concentration of H^+ ions in the system during the inversion of sucrose,



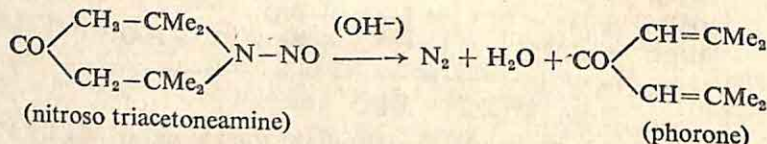
$$\frac{dx}{dt} = k_{H^+} C_{H^+} C_{sugar}$$

where k_{H^+} is the catalytic coefficient for H^+ ions for the reaction. Another reaction in which H^+ ion acts as catalyst is the inversion of menthone. Such reactions which are catalysed by H^+ ions only are said to be subject to *specific hydrogen ion catalysis*.

Similarly there are reactions which are catalysed by OH^- ions only and hence are said to belong to the group of *specific hydroxyl ion catalysis*. As examples we may cite the conversion of acetone into diacetone alcohol or the decomposition of nitroso-triacetoneamine.

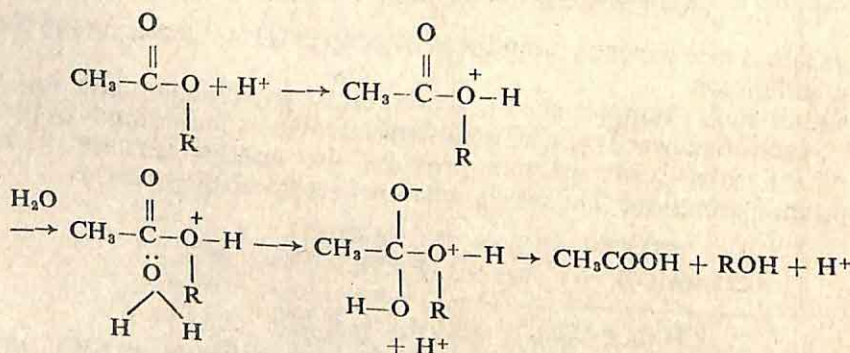


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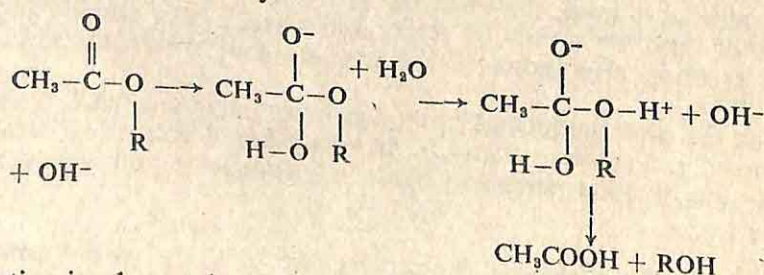


There are however some reactions in which both H^+ ions and OH^- ions simultaneously act as catalysts, probably along with water. The undissociated acid or base have negligible effect. The outstanding example of H^+ and OH^- ion catalysis is that of the hydrolysis of esters. The mechanism of reactions may be expressed as follows :

(a) With H^+ -ion as catalyst



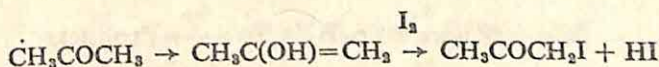
(b) With hydroxyl ion as catalyst



The rate of reaction is adequately expressed as

$$\frac{dx}{dt} = k_{H^+} C_{H^+} C_{ester} + k_{OH^-} C_{OH^-} C_{ester} + k_{H_2O} C_{H_2O} C_{ester}$$

In the beginning of this century Taylor, Dawson and others made a significant observation. Some reactions which were known to be catalysed by H^+ ion seemed to be also influenced by undissociated acid molecules. For examples, the decomposition of diazoacetic ester was catalysed by picric acid. If sufficient picrate were added to the system to reduce the H^+ ion conc. to a negligible value, the rate of reaction was yet appreciably high. It was therefore concluded that the decomposition reaction is catalysed by both H^+ ion and undissociated HA molecules. This idea then called "dual theory of catalysis" was extended to include later all acids, as defined by Brönsted and Lowry, which would have catalytic effect. This is known as *generalised acid catalysis*. The reactions under this category would be catalysed by H^+ , HA and cations of weak bases. Water if present in the system, may act both as an acid or as a base. An example of generalised acid catalysis is the iodination of acetone catalysed by monochloroacetic acid (HA) and its salt.

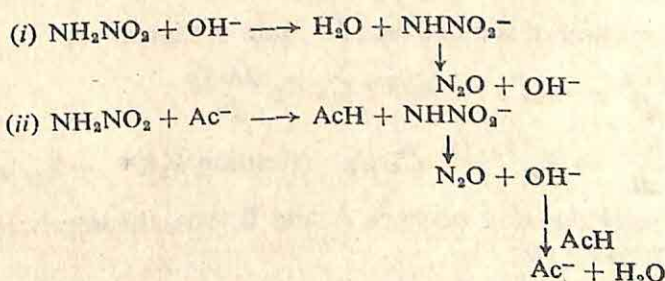


$$\text{The rate of reaction, } \frac{dx}{dt} = k_{H^+} C_{H^+} C_s + k_{H_2O} C_{H_2O} C_s + k_{HA} C_{HA} C_s$$

where C_s is the concentration of the substrate.

By studying the reaction rate with known but different concentrations of acid-salt (catalyst) mixture, it is possible to evaluate the k 's, the catalytic coefficients.

Likewise, there are also reactions which are subject to *generalised base catalysis*. The decomposition of nitramide in solution is catalysed not only by OH^- ion but also by Ac^- , H_2O , etc. The catalytic processes are



The overall reaction rate would be

$$\frac{dx}{dt} = k_{OH^-} C_{OH^-} C_s + k_{Ac^-} C_{Ac^-} C_s + k_{H_2O} C_{H_2O} C_s$$

Finally, there are some reactions such as mutarotation of glucose or the enolisation of acetone, which are subject to *generalised acid-base catalysis*. All acids and all bases including H^+ , OH^- , HA, BOH, and anions of weak acids and cations of weak bases have catalytic effect on these reactions. Schematically, the mutarotation may be expressed as :



The reaction rate will be,

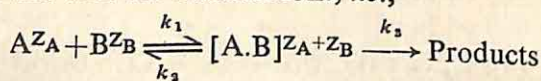
$$\frac{dx}{dt} = k_{OH^-} C_{OH^-} C_s + k_{H^+} C_{H^+} C_s + k_{Ac^-} C_{Ac^-} C_s + k_{HA} C_{HA} C_s + k_{H_2O} C_{H_2O} C_s.$$

The catalytic coefficients determined experimentally for this reaction at $291^\circ K$ are : $k_{OH^-} = 6 \times 10^3$, $k_{H^+} = 1.4 \times 10^{-1}$, $k_{Ac^-} = 2.7 \times 10^{-2}$, $k_{HAc} = 2 \times 10^{-3}$, $k_{H_2O} = 6 \times 10^{-3}$.

That both acids and bases are active in catalysing the process is convincingly demonstrated from the study of mutarotation of tetramethyl glucose. In absence of water, if the reactant is taken in base pyridine the rate is very slow. Similarly if it is taken in acid meta-cresol, there is hardly any mutarotation. But if the

tetramethyl glucose is taken in a mixture of *m*-cresol and pyridine, the reaction is largely catalysed. The reaction thus requires the presence of both an acid and a base—a case of generalised acid-base catalysis.

Primary Kinetic Salt Effect. Due to electrostatic interactions, the kinetics of reaction between ions deviate from those observed in reaction between non-electrolytes. The velocity constants of ionic reactions, it will be seen, depend upon the charges of the reacting ions and also the ionic strength of the solution. The effect of ionic strength (μ) on the rate constant is called the *primary kinetic salt effect*. A very satisfactory treatment of this matter was first made by Brönsted (1922) and later on by Bjerrum. It has been postulated that the ions, say A^{z_A} and B^{z_B} first form an activated complex $(A.B)^{z_A+z_B}$ which subsequently decomposes to yield the products. The complex formed at any time has a small concentration and it is in equilibrium with the reactant ions, *i.e.*,



where z_A , z_B , etc. are the charges of the respective species; k -terms are velocity constants.

The equilibrium constant is given by

$$(1) \quad k \neq = \frac{a_x}{a_A \cdot a_B} = \frac{C_x f_x}{(C_A \cdot f_A)(C_B \cdot f_B)},$$

in which a 's represent activities, C 's concentrations and f 's activity coefficients; the suffix 'x' indicates the complex formed. Rewriting, we have

$$(2) \quad C_x = K \neq \cdot C_A \cdot C_B \cdot \frac{f_A \cdot f_B}{f_x}.$$

Now the rate of formation of the product, *i.e.*, rate of reaction is

$$\frac{dC_P}{dt} = k_3 C_x = k_3 K \neq \cdot C_A \cdot C_B \cdot \frac{f_A \cdot f_B}{f_x}$$

$$(3) \text{ or } \frac{dC_P}{dt} = k_0 \cdot \frac{f_A \cdot f_B}{f_x} \cdot C_A \cdot C_B \quad (\text{Putting } k_3 K \neq = k_0, \text{ constant})$$

But for the bimolecular reaction between A and B ions, the experimental rate of reaction may be expressed as

$$(4) \quad \frac{dC_P}{dt} = k C_A \cdot C_B,$$

where k is the experimentally evaluated rate constant.

Comparing (3) and (4), we have $k = k_0 \frac{f_A \cdot f_B}{f_x}$

$$(5) \text{ or } \log k = \log k_0 + \log f_A + \log f_B - \log f_x$$

Applying Debye-Hückel's relation, the activity coefficients may be expressed in terms of ionic strength i ; $\log f = -0.509 z^2 \sqrt{i}$ at 25°C.

$$\text{Hence, } \log k = \log k_0 - [0.509 z_A^2 + 0.509 z_B^2 - 0.509 (z_A + z_B)^2] \sqrt{i}.$$

$$\text{or } \log k = \log k_0 + 1.018 z_A z_B \sqrt{i}.$$

This is known as Brönsted-Bjerrum equation. A plot of $\log k$ against $\sqrt{i}$ for aqueous solution (25°C) would be linear and its slope would be $1.018 z_A z_B$ and intercept $\log k_0$ (XV.52a)

The plot of $\log k/k_0$ vs. $\sqrt{i}$ would be linear, the slope of the line depending on $z_A z_B$, *i.e.*, the charges of the reacting ions. Three special cases may arise:

(i) When z_A and z_B are of the same sign, $z_A z_B$ is positive, the rate constant would increase with $\sqrt{i}$.

(ii) When z_A and z_B are of opposite sign, $z_A z_B$ is negative, the rate constant would decrease with $\sqrt{i}$.

(iii) When one of the reactants is uncharged, $z_A z_B$ is zero, the rate constant would be independent of i .

These predictions have been confirmed from experimental results. In Fig. (XV.7a), plots of $\log k/k_0$ against $\sqrt{i}$ are given for reactions of ions with different z_A, z_B values. The lines indicate the theoretical predictions from equation XV.52a and the dots are the experimental data.

1. $2[\text{CO}(\text{NH}_3)_5 \text{Br}]^{++} + \text{Hg}^{++} + 2\text{H}_2\text{O} \rightarrow 2[\text{CO}(\text{NH}_3)_5 \text{H}_2\text{O}]^{+++} + \text{HgBr}_2$
2. $2\text{I}^- + \text{S}_2\text{O}_8^{--} \rightarrow \text{I}_2 + 2\text{SO}_4^{--}$
3. Inversion of sucrose solution
4. $\text{H}_2\text{O}_2 + 2\text{Br}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{Br}_2$
5. $[\text{CO}(\text{NH}_3)_5 \text{Br}]^{++} + \text{OH}^- \rightarrow [\text{CO}(\text{NH}_3)_5 \text{OH}]^{++} + \text{Br}^-$

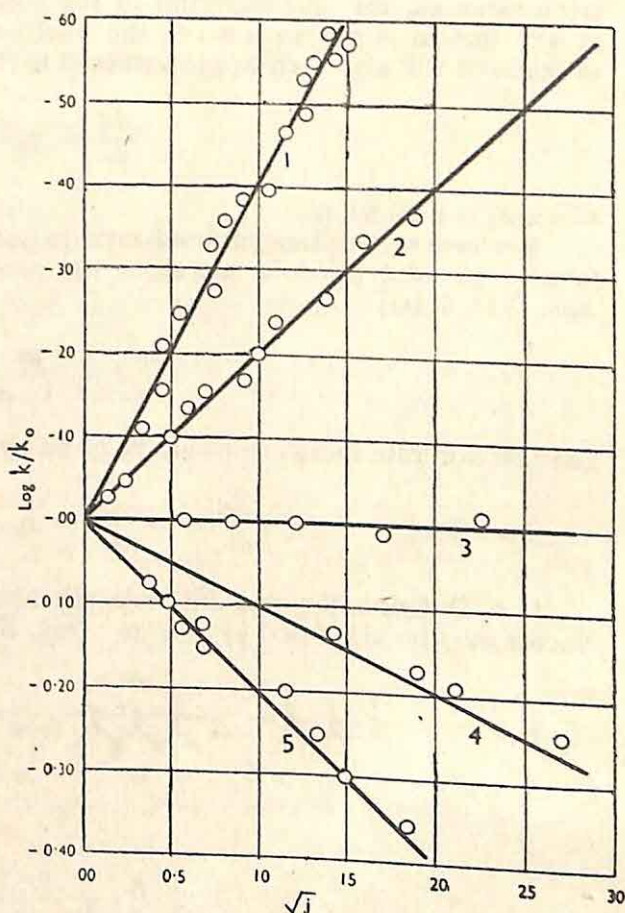


FIG. XV.7a Rate constant variation with ionic strength

XV.24. Heterogeneous Catalysis. In heterogeneously catalysed reactions, a solid serves as a catalyst and the reactants are gaseous in most cases or liquids in others. One or more of these reactants are adsorbed on the surface of the solid catalyst or rather chemisorbed on the surface. This indeed is quite similar to the formation of intermediate complexes with catalysts envisaged in homogeneous catalysis. The adsorbed reactant needs a lower activation energy for transformation and thus provides an alternative path for the reaction to proceed in an accelerated rate. In many cases, the heat of adsorption leads to the activation of the reactant and the reaction takes place easily.

A reaction taking place on a surface is supposed to consist of four consecutive steps :

- (i) Diffusion of gases to the surface
- (ii) Adsorption of the gases on the surface
- (iii) Reaction on the surface
- (iv) Desorption and diffusion of the products from the surface to the bulk.

Of these the diffusion processes (i) and (iv) are generally believed to be rapid and normally do not play any part in the overall rate-determination of the process. The molecules which are adsorbed on the surface are really suitable for undergoing chemical transformation. According to modern thinking, the adsorption and desorption equilibria are easily attained ; it is the concentration of the reactant

molecules on the surface on which the reaction-rate would depend. In its quantitative treatment, the Langmuir concept of unimolecular film on the surface is accepted whereby a complex between the surface atoms and the reactant molecules is formed through valence forces (*i.e.*, chemisorption), as explained in Sec. XIV.4. In such circumstances, the concentration of the adsorbed molecules on the surface layer at any instant is proportional to the fraction of the surface (θ) covered. The rate of reaction will also then be proportional to the covered portion of the surface, *i.e.*,

$$\frac{dx}{dt} = z_1 \theta \quad \dots (XV.53)$$

where z_1 is a constant.

We have seen in Langmuir adsorption isotherm that the fraction of surface (θ) covered by adsorption is related to the pressure (p) of the gas by the relation [eqn. XIV.4(D)]

$$\theta = \frac{ap}{1+ap} \quad \dots (XV.54)$$

The reaction rate therefore would be given by

$$\frac{dx}{dt} = \frac{-dp}{dt} = z_1 \cdot \frac{ap}{1+ap} \quad \dots (XV.55)$$

If A, B denote the reactant molecules and S the surface atom of the solid, the process may be visualised as follows : (Fig. XV.8).

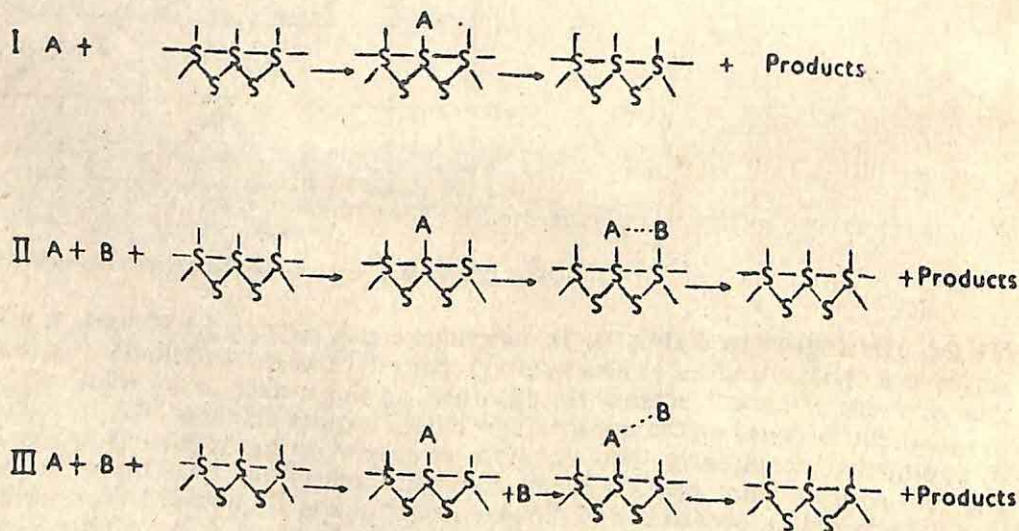


FIG. XV.8

When there is a single reactant, it is first chemisorbed on the surface and subsequently on activation breaks up into products as in (I). But if there are two reactants, the process may occur in two ways. Both the reactants may be adsorbed on adjacent or neighbouring sites on the surface as in (II), or, only one of the reactants may be adsorbed on the surface and the other from the gas-phase may react with the adsorbed one as in (III). These are certainly the most simplified pictures of the transformations. Let us now consider the reaction rates for a few simple cases.

I. *Dissociation of a single substance on a solid surface.* Generally speaking,

the reaction rate,
$$\frac{-dp}{dt} = z_1 \cdot \theta = z_1 \cdot \frac{ap}{1+ap}$$

The kinetics however will be different under different circumstances depending upon the extent of adsorption.

(i) When the adsorption is slight either due to very low pressure or due to the low adsorption-capacity of the surface, (*i.e.*, a is small), or ap becomes negligible compared to unity,

$$\frac{-dp}{dt} = z_1 \cdot ap = k_1 p.$$

On integration,
$$k_1 = \frac{1}{t} \ln \frac{p_0}{p} \quad \dots (XV.56)$$

where p_0 = initial pressure of the gas.

In other words, with low adsorption of the gas, the reaction will behave as one of the *first order*. Instances of such reactions are found in the dissociation of HI on platinum, decomposition of N_2O on gold, decomposition of phosphine on glass, etc.

(ii) When the pressure is very high or the adsorbing capacity of the surface for the reactant is quite high, θ is almost unity, or $ap \gg 1$. In such a condition,

$$\frac{-dp}{dt} = \frac{z_1 ap}{ap} = z_1 \quad \dots (XV.57)$$

i.e., the reaction-rate is constant or independent of pressure. A reaction obeying this relation is called a reaction of *zero order*. Such cases have been observed in the dissociation of HI on gold, ammonia on tungsten.

(iii) When the adsorption is moderate *i.e.*, neither high nor low, the reaction rate is expressed by equation (XV.55), which may be approximated to

$$\frac{-dp}{dt} = k_1 p^n, \text{ where } 1 > n > 0$$

i.e., n will be a fraction. The order of the reaction will be a fractional one, *e.g.*, the decomposition of stibine on antimony has been observed to have a fractional order of 0.6, as

$$\frac{-dp}{dt} = k_1 p^{0.6}.$$

II. Two reactants undergo change on the surface.

Let us now take a reaction in which two molecules A and B react on the surface having occupied neighbouring sites. Suppose θ_1 and θ_2 are the fractions of the surface covered by adsorption of A and B respectively, so that the portion of surface remaining vacant is $(1 - \theta_1 - \theta_2)$.

At equilibrium, the rates of adsorption and desorption of A would be equal. The same will also hold true for B. So,

$$k_1(1 - \theta_1 - \theta_2)p_1 = k'_1\theta_1 \quad \dots (i)$$

and
$$k_2(1 - \theta_1 - \theta_2)p_2 = k'_2\theta_2 \quad \dots (ii)$$

where p_1 and p_2 are partial pressures of A and B.

Dividing (ii) by (i)
$$\theta_2 = \frac{k_2 k'_1 p_2}{k_1 k'_2 p_1} \theta_1 \quad \dots (iii)$$

Substituting (iii) in (i)
$$\theta_1 = \frac{k_1 p_1}{k'_1 + k_1 p_1 + \frac{k_2 k'_1 p_2}{k'_2 p_1}} \quad \dots (iv)$$

and from (ii),
$$\theta_2 = \frac{k_2 p_2}{k'_2 + k_2 p_2 + \frac{k_1 k'_2 p_1}{k'_1 p_2}} \quad \dots (v)$$

The rate of reaction will be $\frac{-dp}{dt} = z\theta_1\theta_2 \dots$ (XV.58)

Three different cases are of special significance.

Case (I). Each gas is adsorbed very slightly, i.e., both θ and θ' are quite small compared with unity. In such an event, the reaction rate will be

$$\frac{-dp}{dt} = z\theta_1\theta_2 = z \cdot \frac{k_1p_1 \cdot k_2p_2}{k'_1k'_2} = k p_1p_2 \dots$$
 (XV.59)

It means the rate will be one of *second order*. Examples of this type are found in the hydrogenation of ethylene on copper or the formation of nitrogen peroxide from nitric oxide and oxygen on glass.

Case (II) When one reactant A is relatively more strongly adsorbed than B. Here θ_1 is much larger than θ_2 , but θ_1 is less than unity. It is easily seen that the term k_2p_2 is negligibly small. Hence equation (iv) and (v) would be,

$$\theta_1 = \frac{k_1p_1}{k'_1 + k_1p_1}$$

and

$$\theta_2 = \frac{k_2p_2}{k'_2 + \frac{k_1k'_2p_1}{k'_1}} = \frac{k'_1k_2p_2}{k'_2(k'_1 + k_1p_1)}$$

Hence
$$\frac{-dp}{dt} = z\theta_1\theta_2 = \frac{z \cdot k_1k'_1k_2 \cdot p_1p_2}{k'_2(k'_1 + k_1p_1)^2} = k \cdot \frac{p_1p_2}{(1 + bp_1)^2} \dots$$
 (XV.60)

where

$$b = k_1/k'_1$$

Such a complicated kinetics is being followed in the reaction between CO_2 and H_2 on platinum.

Case. (III) When one reactant is very strongly adsorbed.

We have,
$$\theta_2 = \frac{k_2k'_1p_2}{k_1k'_2p_1} \theta_1 \quad (\text{vide eqn. iii}).$$

Therefore, reaction rate is

$$\frac{-dp}{dt} = z \cdot \theta_1\theta_2 = z \cdot \theta_1 \cdot \frac{k_2k'_1p_2}{k_1k'_2p_1} \theta_1, \quad \text{where } \theta_1 \text{ is almost unity.}$$

Since $\theta_1 \approx 1$,
$$\frac{-dp}{dt} = k \cdot \frac{p_2}{p_1} \dots$$
 (XV.61)

The reaction between CO and O_2 on platinum follows such a kinetics.

XV.25. Negative Catalysis and Inhibition. It is evident from eqn. (XV.61) that higher is the pressure p_1 and hence higher the adsorption of the component A, lower will be the reaction rate. That is, the component which is very strongly adsorbed inhibits the reaction.

Sometimes the products of the reaction are also adsorbed by the surface of the catalyst. There is a competition between the reactant and product molecules for the available surface of the catalyst for adsorption. For example, in the dissociation of ammonia, $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$, on platinum filament there is a keen rivalry

between NH_3 and H_2 for the surface, the latter being strongly adsorbed. This is similar to case (iii) above, and following same argument, the reaction kinetics is given by

$$\frac{-dp}{dt} = k \cdot \frac{p_{\text{NH}_3}}{p_{\text{H}_2}}$$

Sometimes small amounts of foreign substances inhibit or retard the reaction rate appreciably. These are called *poisons*. These may function in different ways. In most cases, poisons are adsorbed on the portions of the surface which would otherwise have been catalytically active in carrying out a reaction. In some cases, the poisons may form definite chemical compounds with the catalyst atoms. For example, minute quantities of arsenic totally destroy the catalytic activity of platinum by forming platinum arsenide at the surface, in the H_2SO_4 manufacture.

Negative catalysis or inhibition has also been observed in many homogeneous reactions. To illustrate : autoxidation of sodium sulphite solution in air is retarded by the presence of small amounts of glycerine, ethyl alcohol, benzaldehyde, mannitol, etc. Similarly the auto-oxidation of benzaldehyde is strongly inhibited by traces of some sulphur compounds.* In some cases, there is definite evidence that the inhibitor combines or removes the positive catalyst and thus the reaction rate is lowered. Cu^{++} ion is a strong positive catalyst for autoxidation of sodium sulphite solution. If traces of KCN be added to the system, the reaction is almost stopped as CN^- forms a complex with the catalytically active Cu^{++} catalyst, (Titoff, 1903). On the other hand, there are reactions which normally proceed with a chain-mechanism and the function of the inhibitor is simply to break the chains thereby retarding the process. Backström and Alyea showed that traces of anthracene almost completely prevents auto-oxidation of benzaldehyde by breaking the chains. The rate of reaction with a concentration C_i of the inhibitor is given usually by

$$\text{Rate} = \frac{k}{k' C_i + k''}$$

(see also eqn. XV.52).

Sodium arsenite solution is not oxidised in air but if this solution is kept in air mixed with sodium sulphite solution both of them are oxidised. Such cases are called "*Induced Reactions*"; sodium arsenite is oxidised by induction. It is believed that sodium arsenite is really involved in breaking the chains of sodium sulphite oxidation and in this act it combines with the chain carriers leading to its own oxidation.

XV.26. Effect of Temperature on Surface Reactions. It has been mentioned earlier that adsorption of reactants on the surface provide an alternative path for the reaction with a lower energy of activation. In chemisorption appreciable amounts of heat of adsorption are evolved. The adsorbed reactant molecules become sufficiently energy-rich with a partial distortion of internal bonds. In consequence, a smaller amount of energy is required for the formation of the activated complex. It is hence expected that the activation energy for the surface reaction would be much less than that for the corresponding homogeneous reaction.

With the application of the Arrhenius equation and plotting $\log k$ against $1/T$, the activation energy (E_a) is evaluated for the heterogeneous reaction. The activation energy, E_a , so obtained is called the *apparent activation energy*. Since the extent of adsorption is temperature-dependent, E_a evaluated is indeed the algebraic sum of the true activation energy (E_t) of the reaction and the heats of adsorption of the reactant and resultant (λ), such that

$$E_a = E_t - \lambda_{\text{reactant}} + \lambda_{\text{product}}$$

In the table below are given the activation energies of some reactions occurring in homogeneous and in heterogeneous conditions. The results indicate that in every case, the activation energy in the heterogeneous process is considerably less than that in the homogeneous process.

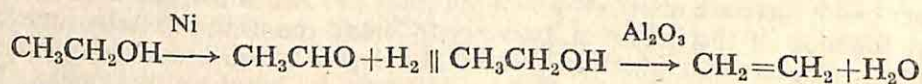
*The brisk decomposition of H_2O_2 solution in presence of small amounts of FeCl_3 is considerably retarded or arrested if a pinch of NaNO_2 or acetanilide be added.

TABLE : ACTIVATION ENERGIES IN HOMOGENEOUS AND HETEROGENEOUS REACTIONS

Reaction Decomposition of	Surface	Activation energy (K cal)	
		Heterogeneous	Homogeneous
HI	Gold	14.0	44.0
CH ₄	Platinum	57.0	80.0
NH ₃	Gold	29.0	58.5
N ₂ O	Tungsten	39.0	80.0

XV.27. The Nature of the Surface. It has to be realised that adsorption does not necessarily lead to catalytic reaction but that surface-catalysed reactions always occur through adsorption. The surfaces which are catalytically active have some interesting features.

In their catalytic functions, surfaces are specific in nature. A surface which catalyses the cracking of an oil may not at all influence the dehydration of alcohols. For different reactions, different catalytic surfaces are effective. Nickel and copper surfaces are very good catalysts for hydrogenation processes whereas alumina is a suitable catalyst for dehydration processes. This is due to the fact that hydrogen is strongly adsorbed on Ni or Cu-surface, and water molecules are strongly adsorbed on alumina surface. As a result when ethanol vapour is passed over Ni-catalyst it is oxidised to acetaldehyde but when it is passed over alumina, it is dehydrated to ethylene :



These may be represented as in Fig. XV.9 : (Alumina has both oxygen atoms and OH groups on the surface).

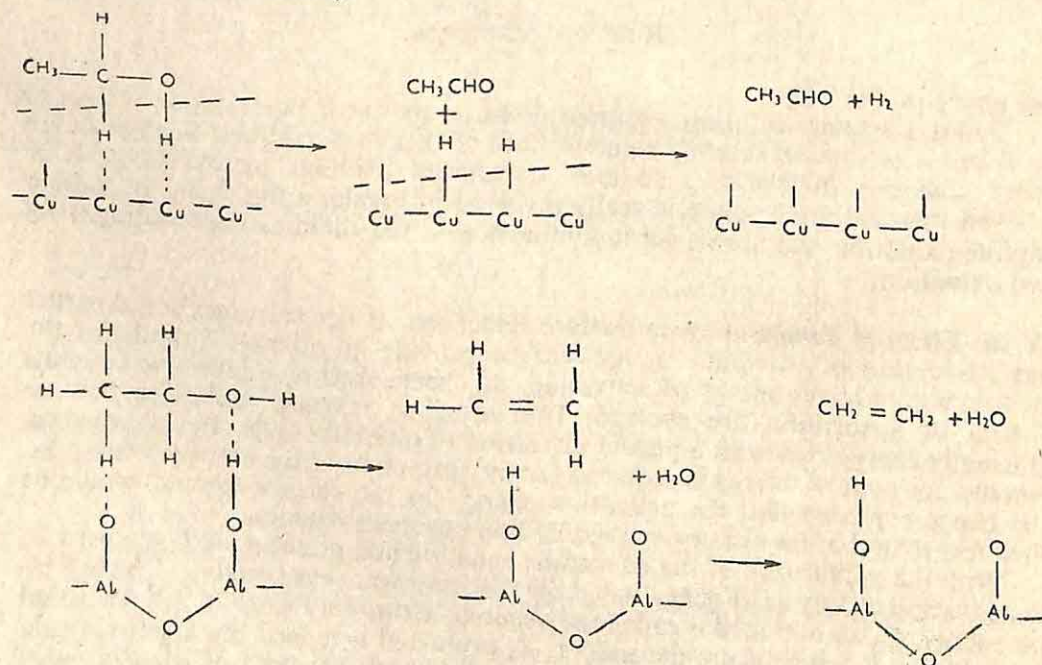
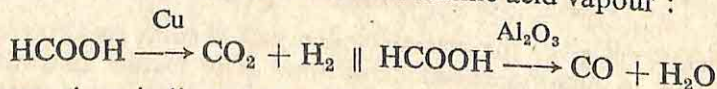


Fig. XV.9

Similar alternative reactions are seen with formic acid vapour :



These observations indicated that there must be some definite orientation of the adsorbate on a given surface. Palmer and Constable showed that the rate of dehydrogenation of five primary alcohols, ethyl, propyl, butyl, etc. on copper surface was the same and independent of the length of the hydrocarbon-chain. But the

rate of decomposition of a secondary alcohol was much higher. This confirms the orientation of the molecules in adsorption. Some of the catalysts which are commonly used in different types of reactions are listed below.

Processes	Catalysts
(i) Hydrogenation/dehydrogenation	Ni, Cu, ZnO-Cr ₂ O ₃
(ii) Dehydration/hydration	Al ₂ O ₃
(iii) Cracking of petroleum fractions	SiO ₂ -Al ₂ O ₃ gel
(iv) Synthesis of ammonia	Iron
(v) Polymerisation	Al(Et) ₃ , TiCl ₄ , phosphoric acid on keiselguhr

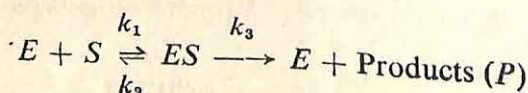
The physical nature of a surface also influences its catalytic efficiency. Theoretically a surface may be regarded quite smooth and plane and every elementary space in it can adsorb an adsorbate-molecule. But in fact, even the smoothest surface is sufficiently rough and have many irregularities. There are on the surface peaks, edges and corners, furrows and craters, cracks etc. at least on a scale of 5–10 Å. Such a state has also been confirmed from multiple beam interferometric experiments and from studies of thermionic emission from different parts of the surface. It is therefore easily understood that the "residual field" of the surface atoms is not uniform throughout the surface. Those atoms which are at the peaks, edges etc. have high residual fields and are likely to have greater adsorption capacity. In 1925 Taylor postulated that the adsorption and subsequent reaction take place preferentially on certain parts of the surface, which he called "active centres". The active centres may constitute a small portion only of the total surface sites.

Moreover all active centres where adsorption occurs are not always catalytically effective. For example, ethylene and hydrogen are both adsorbed on copper surface and react to produce ethane. A trace of Hg-vapour reduces the adsorption of ethylene to 80% and that of hydrogen to 5%. But the catalytic efficiency is reduced much more and only 0.5% of the initial efficiency is observed. It leads to two inevitable conclusions : (i) Different gases are adsorbed on different parts of the surface and (ii) the catalytic activity is confined to a small fraction of the active centres.

The same conclusion was also arrived at from other observations. Peace (1923) found that traces of CO quite insufficient in amount to cover the entire copper-surface or to displace the hydrogen adsorbed on it can completely inhibit the reaction between hydrogen and ethylene. Again Hinshelwood observed that a Pt-wire on which hydrogen had already been strongly adsorbed would not catalyse the decomposition of ammonia but would remain unaffected for the dissociation of HI. It showed that the active centres for ammonia and hydrogen iodide were different.

XV.28. Enzyme Catalysis. Enzymes are complex protein substances produced by living cells. These are responsible for catalysing infinite types of chemical changes occurring in living processes. Even when these enzymes are isolated from the cells, they retain their catalytic activity and function in the same fashion *in vitro*. Enzymes are often present in colloidal state and are extremely specific in their catalytic functions. Thus, *catalase* obtained from some plant cells catalyse the decomposition of H₂O₂ only, *zymase* from yeast would ferment dextrose but will be ineffective in the breakdown of starch or cane sugar, *urease* hydrolyses urea but not methyl urea or a protein.

The mechanism of an enzymatic process is represented in the following way. The enzyme (*E*) first forms a complex intermediate with the substrate (*S*). The amount of enzyme is very small compared to the amount of the substrate. The intermediate complex (*ES*) then decomposes into the products reproducing the enzyme. The processes may be represented as,



When smooth reaction begins, the rate of change of (ES) is given by

$$\frac{d[ES]}{dt} = k_1[E][S] - k_2[ES] - k_3[ES]$$

the brackets indicating the respective concentrations.

Applying steady-state principle, the conc. of the complex would be small and constant, hence

$$\frac{d[ES]}{dt} = k_1[E][S] - (k_2 + k_3)[ES] = 0.$$

If $[E]_0$ is the total molar concentration of the enzyme and the rate is measured when the change in the concentration of the substrate is not large, we have

$$[E]_0 = [E] + [ES]$$

$$\therefore k_1([E]_0 - [ES])[S] - (k_2 + k_3)[ES] = 0$$

$$\text{or } [ES] = \frac{k_1[E]_0[S]}{k_1[S] + (k_2 + k_3)} = \frac{[E]_0}{1 + \frac{k_2 + k_3}{k_1} \cdot \frac{1}{[S]}}$$

The rate of formation of the products is

$$\frac{d[P]}{dt} = k_3[ES] = \frac{k_3[E]_0}{1 + \frac{k_2 + k_3}{k_1} \cdot \frac{1}{[S]}} \quad \dots (XV.62)$$

where $\frac{k_2 + k_3}{k_1}$ is called *Michaelis constant*, the rate equation indicates that the reaction is of the first order with respect to enzyme concentration; and further when $[S]$ is very high, the reaction would be of zero-order with respect to substrate. Experimental measurements have confirmed these expectations.

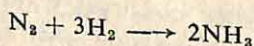
The enzyme as a catalyst is unique. The catalytic activity or turnover number is exceedingly large in the case of enzyme catalysts. Thus, in the decomposition of H_2O_2 , the turnover numbers (n) are as follows.

Catalyst	$\log_{10} n$ per iron atom
$Fe(OH)_3$	10^{-4}
Hematin	10^{-1}
Catalase	10^6

It is now firmly held that enzymes are possessed of an active site or active centre, through which they form the complex.

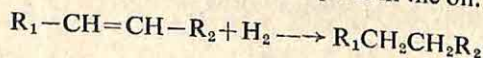
XV.29. Industrial Catalysis. The most important applications of catalysis are in the large scale production of various substances in industry. Some of these are named below.

(i) Synthesis of ammonia: Catalyst is iron, often mixed with small amounts of K_2O and Al_2O_3 as 'promoters'.

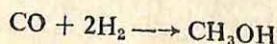


Promoters are substances which increase the catalytic efficiency of the catalyst but these substances themselves need not be catalytic. A very clear explanation of the function of promoters is not available; it is usually believed that promoters increase the active centres by introducing discontinuities on the surface.

(ii) Hydrogenation of oils: Nickel catalysts and sometimes metal-oxide catalysts are extensively used for saturating the unsaturated aliphatic acid parts in the oil.

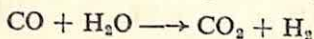


(iii) Synthesis of methanol:

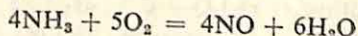


The catalyst employed is zinc oxide-chromium oxide for this very successful industrial operation. [Cr_2O_3 is really a promoter.]

(iv) Manufacture of hydrogen : Hydrogen from coke-oven gas and water-gas is obtained by mixing them with steam and passing over the catalyst ferric-oxide :

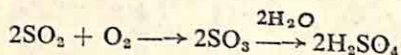


(v) Nitric acid from ammonia :



This reaction is usually carried out in presence of Pt-gauze as catalyst. Sometimes ferric and bismuth oxides are used in place of platinum.

(vi) Manufacture of H_2SO_4 :



The oxidation of SO_2 is carried out on the surface of platinised asbestos.

(vii) Synthesis of hydrocarbons : Liquid fuels are now synthesised by Fischer-Tropsch method from coal, CO , CH_4 , etc. and hydrogen, using cobalt or iron as catalysts.

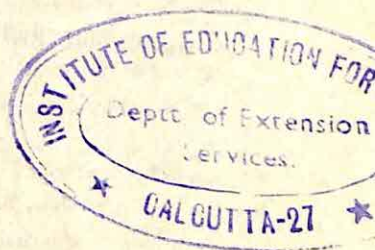
(viii) Cracking of petroleum : This is carried out to increase the yield of gasoline or for producing butadiene, isooctane etc. from petroleum products. Various catalysts including some oxides are commonly used for this purpose.

(ix) Manufacture of ethanol : This industry is essentially based on enzyme catalysis. Zymase is used for the reaction.

Innumerable other instances can be added to the above list.

References for further reading

- (i) Chemical kinetics—Laidler
- (ii) The theory of rate processes—Glasstone, Laidler, Eyring.
- (iii) The foundations of chemical kinetics—Benson
- (iv) Kinetics of reactions in solution—Molwyn-Hughes
- (v) Kinetics and mechanism—Frost and Pearson
- (vi) Kinetics of chemical change—Hinshelwood
- (vii) Chemical kinetics and chain reaction—Semenoff
- (viii) Free radicals—Steacie
- (ix) Acid-base catalysis—Bell.



Problems

1. In the inversion of cane sugar the polarimetric readings were :

t (min)	0	30	90	330	∞
Readings	+46.75	+41.00	+30.75	+2.75	-18.75

Find the order of the reaction and the value of the velocity constant.

2. In the thermal decomposition of malonic acid, $\text{CH}_2(\text{COOH})_2 \rightarrow \text{CH}_3\text{COOH} + \text{CO}_2$, the pressures at different time intervals are

t (min)	10	20	35	56	∞
p (mm)	37	67	108	155	303

What is the order of the reaction?

3. In a certain first order reaction, half the reactant was decomposed in 500 seconds. How long will it be until one-tenth is left?

4. At a certain temperature the half-life periods for the decomposition of ammonia in contact with tungsten were as follows :

p (mm)	50	100	200
Relative half-life period	3.52	1.82	0.93

Find the order of the reaction.

5. In the reaction between KOH and C_2H_5Br equal quantities of N/10 solutions of each were used. 20 c.c. of the reaction mixture were withdrawn at regular intervals and titrated against N/20 acid. The following data were obtained :

t (min)	0	21	46	97	146
volume of acid (c.c.)	20.00	14.71	11.14	7.42	2.92

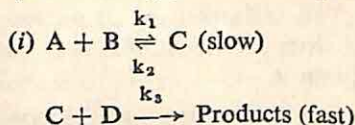
Find the order of the reaction

6. In the thermal decomposition, $(CH_3)_2O \rightarrow CO + H_2 + CH_4$, the initial pressure is given by 'a' mm, and x mm increase in pressure in t seconds. The readings at two temperatures $504^\circ C$ and $552^\circ C$ are as follows :

I. Temp $504^\circ C$; $a = 312$ mm	t (sec)	320	771	1195	2030	3155	∞
	x (mm)	96	176	250	368	467	619
II. Temp $552^\circ C$ $a = 420$ mm	t (sec)	114	219	299	543	∞	
	x (mm)	323	534	634	778	838	

Determine the order of the reaction and the mean velocity constants at these two temperatures. Calculate also the mean energy of activation. What will be frequency factor at $504^\circ C$?

7. On the basis of stationary state concept, obtain an expression for the rate law of the process.



8. For the reaction, $H_2O_2 + 2H^+ + 2Br^- \rightarrow 2H_2O + Br_2$, the rate law is given by

$$-\frac{dC_{H_2O_2}}{dt} = kC_{H_2O_2}C_{H^+}.C_{Br^-}.$$

At $298^\circ K$, k varies with hydrogen bromide concentration as follows :

C_{HBr} (millimoles/litre)	13.5	22.0	28.8	43.2	67.7
$k \times 10^3$ ($l^2/\text{mole}^2 \text{ min}$)	377	346	340	318	298

Plot graphically and show that uncatalysed reaction will have the rate constant $k_0 \times 10^3 = 466$

9. At $427^\circ C$, the thermal decomposition of a gas was found to be of first order and the half-life period is 300 min and the energy of activation is 50000 cal/mole. Find out the time necessary for the gas to be decomposed 60% at $527^\circ C$.

10. The specific reaction rate for the decomposition of N_2O_5 is given by $k = 4 \times 10^{13} e^{-25000/RT}$. Find out (a) the half-life at $0^\circ C$ and (b) time required for 60% decomposition at $77^\circ C$.

11. For a reaction, $A \rightarrow B$, the rate constant is given by

$$k = 1.2 \times 10^{-3} \text{ litre/mole-sec. at } 87^\circ C$$

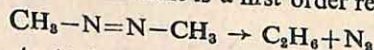
and the energy of activation, $E_a = 32000$ cal/mole. Estimate the values of (i) $\Delta H^\ddagger$, (ii) $\Delta S^\ddagger$.

12. In an isomerisation process, the following first order rate constants were found,

Temp ($^\circ C$)	120°	130°	140°
k (sec^{-1})	5.0	11.5	26.4

Calculate (i) energy of activation, (ii) frequency factor and (iii) the entropy of activation.

13. The decomposition of azo-methane is a first order reaction

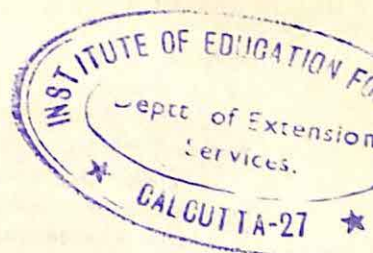


with a rate constant, $k = 4 \times 10^{-4} \text{ sec}^{-1}$ at $320^\circ K$.

If initially azomethane is taken at 200 mm pressure, what will be the partial pressures of the components of the system after half an hour ?

$$[Ans : P_{azo} = 98 \text{ mm}, P_{C_2H_6} = P_{N_2} = 51 \text{ mm}]$$

THE COLLOIDAL STATE



XVI.1. The Colloidal System. The subject of colloidal system had a diffuse beginning. Various stray and independent investigations carried out by Richter, Berzelius, Selmi, Graham and others in the nineteenth century yielded results from which systematisation followed to form, in the early part of the present century, a sort of nucleus around which the science of colloidal system developed and rapidly proliferated.

Substance like sand, powdered glass, barium sulphate etc. when added to water sink to the bottom of the container ; others such as naphthalene powder, charcoal etc. when added remain afloat in water as a distinct phase. This is not only true for water as the medium but for many other solvents as well. On the other hand lumps of sugar or salt in water or naphthalene in benzene form true solutions in which the phase distinctions between the components—solutes and solvents—are obliterated.

Between these extremes of heterogeneous coarse suspensions and homogeneous true solutions, exist systems with properties intermediate between those of the former two. Besides, these systems have sets of properties which can be called as characteristically theirs only. Examples of such systems are provided by suspensions of gum in water, fine suspension of soil in water, suspension of NaCl in alcohol or of arsenious sulphide in water. That these suspensions are really different from true solutions can be shown by allowing them to percolate through parchment or cellophane papers, as Graham did. The true solutions will get through, but these set of suspensions will not ; only the continuous medium water or benzene etc. will seep through. But these suspensions pass through ordinary filter paper like true solutions. The solute particles in true solutions are molecularly dispersed ($\sigma = 10^{-8}$ cm approx) and are invisible. In the case of these fine suspensions, the particles are bigger (σ between $10^{-7} \sim 10^{-4}$ cms approx) and can be seen either with the help of a high powered microscope or at least can be indirectly discerned utilising some optical effect (Tyndall effect).

Substances in such a state of subdivision and suspended or dispersed in a continuous medium as to demonstrate the above effects are said to be in the colloidal state. The colloidal system, often called a *sol*, would thus consist of a dispersed phase (gum etc.) in dispersion medium (water, benzene etc). A rigorous definition of a colloidal system is difficult to lay down, a workable definition can be given in the following words :

"A colloidal system is a two-phase heterogeneous system in which one phase is dispersed in a fine state of subdivision (ranging from 1μ to $50 m\mu$ approx) in another medium termed the continuous or dispersion medium. In actual instances, the size limits are not rigid and may vary on either side but most systems conform to the above description.

Although we shall be dealing chiefly with colloidal systems in which the disperse phase is a solid and dispersion medium a liquid such as a sol of As_2S_3 in water, the dispersion medium may also be a gas, a liquid or a solid. In *foams*, we have a gas dispersed in liquid, whereas in *smokes* the disperse phase is a solid in gas medium. In *fogs* liquid is dispersed in gas medium. When a liquid is dispersed in another liquid, it is often called an *emulsion* as in milk. Ruby glass or carbon in steel are examples of one solid dispersed in another solid.

XVI.2. Preparation of Colloidal Systems. The preparation of a sol usually involves three operations :

(i) To obtain the substance directly or indirectly in the desired state of fine division in the dispersion medium ;

(ii) To add protective or stabilising agents to maintain the stability of the system. In many instances, however, the protective agents are inherently present in the reagents used in obtaining the finely divided substance in process (i). In other cases, stabilising agents are to be specially added.

(iii) To purify the colloidal system from excess of reagents used or by-products formed by suitable techniques.

There are two general ways (a) *Condensation method* and (b) *Disintegration or dispersion method*, in which a disperse phase can be formed in a medium.

(a) **Condensation Methods.** It is an indirect process for the preparation of a sol. The substance which is to be dispersed is generated *in situ* by some chemical reaction (or sometimes by physical change) under controlled conditions of temperature, concentration, agitation etc. to form insoluble particles of the substance having sizes within the colloidal range. The chemical reactions may be different in different cases, such as oxidation, reduction, hydrolysis, metathesis, etc. Certain specific examples rather than a description in general terms will clarify the procedures.

Gold Sol. A gold sol is conveniently prepared by *reduction* of chloroauric acid say with formate or hydrazine.

Sulphur Sol. Sulphur sols are easily obtained by *oxidation* of H_2S solution by oxygen or SO_2 or some dilute oxyacid and then purified.

When a solution of sulphur in alcohol is poured into water a sulphur sol is formed. The addition of a solution of a substance to a solvent in which the solute is insoluble is often a convenient process of preparing a sol.

Nickel Sol. When a benzene solution of nickel carbonyl is heated, a fine nickel sol is obtained through the *dissociation* process, $\text{Ni}(\text{CO})_4 \rightleftharpoons \text{Ni} + 4\text{CO}$.

Silver iodide Sol. To a suitably dilute solution of KI is added AgNO_3 solution in a quantity appreciably less than the stoichiometric requirement. Silver iodide, produced by *metathesis*, has particle sizes in the colloidal domain and the whole system is stabilised by a small amount of iodide ions present in solution. The unwanted excess of all ions are removed during subsequent purification by dialysis as described later.

Similar metathetical processes are employed in many instances, such as in preparation of BaSO_4 sol from $\text{Ba}(\text{SCN})_2$ and $(\text{NH}_4)_2\text{SO}_4$; As_2S_3 from As_2O_3 and H_2S ; silicic acid sol from sodium silicate and hydrochloric acid etc.

Ferric oxide Hydrosol. When small quantities of ferric chloride are added intermittently to almost boiling water, ferric hydroxide is formed in colloidal state. Small quantities of ferric ions, and possibly hydrogen ions stabilise the sol. The excess of hydrochloric acid formed is removed during the purification of the sol. Many such oxide hydrosols, such as aluminium oxide, tin oxide, thorium oxide etc. are prepared by similar hydrolysis of their chlorides or nitrates.

(b) **Dispersion Methods.** This technique is a direct method and consists in finely pulverising the substance to be dispersed in the medium which is to constitute the dispersion phase. Sometimes the pulverisation is spontaneously effected; for instance, when gelatine is heated in water with stirring, gelatine sol is produced. Sols of agar, gum-arabic, etc. are obtained in the same fashion and no stabilising agents need be added nor any purification necessary.

In certain instances, pulverisation to the colloidal range is done through electric sparking. For example, dilute sols, of gold, silver, platinum etc. are prepared by bringing close two electrodes of the metal concerned under water so as to permit electric discharge between them. Fine particles of the metal in the colloidal range are formed by this process. Employing the same technique, using alternate electrodes of inorganic compounds dipped under water or organic solvents, different hydrosols or organosols were prepared by Svedberg.

Freshly precipitated substances in some cases can be brought to the colloidal state by shaking with small quantities of suitable reagents or sometimes by continued washing with water alone. Thus, freshly precipitated $\text{Fe}(\text{OH})_3$, if shaken with a dilute solution of FeCl_3 , would give rise to ferric oxide sol. This process of dispersing a fine precipitate into colloidal state by adding a little specific electrolyte is called *peptisation*. Freshly precipitated tungstic oxide or vanadium oxide will turn into a sol on continued shaking or washing with water.

Dispersion is also sometimes carried out by the use of atomiser as in the dispersion of a liquid in a gas. "Colloid mills" are also used in mechanically grinding a solid dipped in the dispersion medium.

Purification of Sols. The final stage in sol preparation is its purification.

Not all sols, as mentioned earlier, need this purification process. Even for those systems where purification is imperative, it is carried out only to a certain limit as complete purification induces instability of the sol.

The property common to all sols, namely the inability of the disperse phase to percolate through some membranes such as parchment paper, cellophane etc. where as the dispersion medium, free ions, molecules in solution etc. can easily get through, is taken advantage of in purifying a sol. The most commonly employed techniques are dialysis and electrodialysis.

Dialysis. The sol to be purified is taken in a parchment paper or cellophane bag which is kept suspended in a basin containing sufficient amount of water (or the dispersion medium of the sol if it be not water), as in Fig. XVI.1. The unwanted ions in the sol move out through the cellophane wall while some amount of solvent from outside may enter the bag. From time to time, the solvent in the basin is replaced and the process allowed to continue for several days. To check the extent of purity, small portions of the sol are pipetted out and its electrical conductance is measured. When the conductance reaches a sufficiently low limit as desired by the experimenter, the process is stopped. For reasons to be described later, extreme purification induces instability of the sol. Such a process of separation or removal of soluble ions through a partially permeable membrane is called *dialysis*. In certain sols, as in Al_2O_3 hydrosol, the disperse phase is too small to be retained by cellophane paper. In such cases, dialysis is carried out at somewhat higher temperatures with controlled heating. The particles thereby grow bigger in sizes.

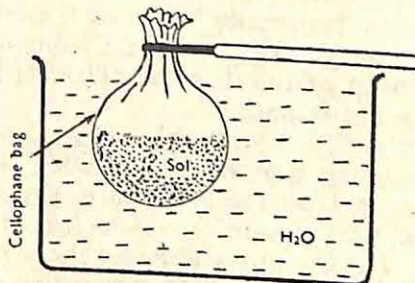


FIG. XVI.1 Dialysis

Electrodialysis. To accelerate the process of purification and also to achieve a greater degree of purity sometimes the dialysis is carried out in a direct current electric field; the process is then called electrodialysis.

A simple electrodialyser consists of three detachable chambers A, B, and C. The middle chamber B which contains the sol is separated on either side from

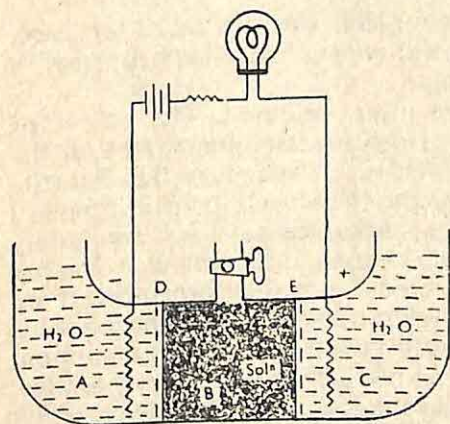


FIG. XVI.2 Electrodialyser (diagrammatic)

A and C by partitions of cellophane paper D and E. (Fig. XVI.2). The side-chambers A and C are filled with water in which are inserted two Pt-gauze electrodes. A 220-volts direct current field is applied to the system with a carbon-filament bulb in series. On passing electric current, the ionic impurities travel outwards, cations to the negative electrode and anions to the positive. For hastening the process, the water in A and C are drawn out from time to time and replaced afresh. With gradual removal of ions, the resistance increases and the fall in current strength is revealed from the bulb in circuit. The process is stopped when a certain degree of purity is attained.

XVI.3. Classification of Colloid Systems. The colloidal systems are sometimes classified into two broad groups : (1) Reversible sols and (2) Irreversible sols. In the reversible sols, the disperse phase is spontaneously distributed in the surrounding medium due to thermal energy. Such spontaneous distribution leads to some equilibrium size distribution corresponding to minimum value of thermodynamic potential. The reversible sols are characterised by very low interfacial tension and hence interfacial energy, 0.01 ergs/cm^2 approx. Once the disperse phase is thrown out of colloidal state its redispersion is easily achieved.

The irreversible sols are thermodynamically unstable ; these have a natural tendency to be thrown out of the dispersion medium from the colloidal state to the macrostate. The concept of their colloidal stability is a kinetic one. It is with considerable difficulty that the substance in such cases are taken into the colloidal state.

But the more common way of classifying the colloids is to divide them into two groups (a) *Lyophobic* and (b) *Lyophilic* sols. Lyophobic sols are those which have no spontaneous tendency to pass into the colloidal state and are obtained with difficulty ; hence these are irreversible in character *e.g.*, gold, As_2S_3 etc. Lyophilic sols are quite easily formed by the spontaneous dispersion of a substance in the dispersion medium ; these are reversible and even if thrown out of medium, they easily revert back to the colloidal state, *e.g.*, gums, starch etc. There are other properties by which these two groups of sols are distinguished.

(i) Very small amounts of neutral electrolyte solutions bring about precipitation of the disperse phase in lyophobic sols, but have hardly any effect on the lyophilic ones.

(ii) Lyophobic sol particles carry charges, either positive or negative, and migrate towards the proper electrode when placed in an electrical field. The charges on the lyophilic sol particles are not conspicuous, though truly lyophilic sol particles do move towards one electrode or the other slowly.

(iii) The viscous properties of the two groups are widely different. Lyophilic sols have very high viscosities whereas the lyophobic ones have viscosity almost equal to that of the dispersion medium. The lyophobic sols can be obtained only in small concentrations but lyophilic ones can be prepared at high concentrations. The disperse phase particles are often highly solvated in lyophilic systems but not so in lyophobic ones.

Sols of AgI , SnO_2 , Pt , etc. are all lyophobic in character where as agaragar, gum arabic, etc. are lyophilic. Examples are also available where the systems belong to the border line. Ferric hydroxide, chromic hydroxide sols are pronouncedly lyophobic but these also possess a certain amount of lyophilicity. Sols are called *hydrophobic* and *hydrophilic* when the medium is water.

XVI.4. Properties of Lyophobic Sols. The lyophobic sols are characterised by many unique properties which are studied mainly under three heads, optical properties, electrical properties and kinetic properties.

The optical and electrical properties of lyophobic sols are taken up here. The kinetic behaviour of the lyophobic systems will be dealt with later along with lyophilic sol properties with which these are similar.

Optical Properties. The lyophobic sols are often coloured. The colour of the sol depends on the size of the particles in suspension and sometimes on the shape also. Thus, a gold sol is red when the particles are extremely fine but the sol is blue when the dispersed particles are bigger. But the most important property of lyophobic sols is the scattering of light by the suspended particles, commonly known as the *Tyndall effect*. Visible light has wave lengths spanning over $350\text{ m}\mu$ and $100\text{ m}\mu$ approximately and these are scattered when they are incident on material particles of sizes commensurate with their wave lengths. The result is that when a beam of visible light is passed through a pure liquid or a true solution, the light is partly absorbed and partly transmitted and there is scarcely any scattering. But when the beam is passed through a lyophobic colloidal system in which the dispersed particles have dimensions generally falling within and a little beyond the visible light wavelength range, the rays are scattered. A strong narrow beam is allowed to pass through a colloidal system situated in a dark background, bright specks or flashes of light become visible when viewed from above through a microscope against the darkness. The specks of light are continuously changing in the system, but also the scattering by the particles and their continuous kinetic movement. Tyndall investigated the scattering properties of colloidal suspensions and this is usually known as the Tyndall phenomenon. He found the scattered beam to be polarised and the intensity of the same to be dependent on the position of the observer, nature of the system, the wavelength of the light used etc.

A quantitative expression of the intensity of scattered light (I) at a distance x from the sol for an incident beam of wavelength λ is given by

$$I = \frac{9\pi n r^6 A^2}{x^2 \lambda^4} \cdot \left(\frac{n_1^2 - n_2^2}{n_1^2 + 2n_2^2} \right)^2 (1 + \cos^2 \theta)$$

where n is the number of dispersed particles per c.c., A is the amplitude and θ is the angle of inclination of the direction of observation with the direction of incident beam, r is the radius of the suspended particles. The refractive indices of disperse phase and dispersion medium are represented by n_1 and n_2 .

Quantitative study of Tyndall effect, and in fact, of other optical and kinetic properties, has been rendered possible with the help of ultra-microscope, first employed by Zsigmondy (1903). The visibility of colloidal particles by microscopes is limited by the aperture of the microscope and the wavelength of light used. Even with very good microscopes and with yellow light, the visibility limit is approximately 2×10^{-5} cms. Zsigmondy showed that if the colloidal particles are illuminated by a strong beam from a direction at right angles to the direction of observation through the microscope (M) and the colloidal particles be observed against a dark background as in Fig. XVI.3 the particles become visible as self luminous specks, regardless of dimensions, due to scattering of light. This is the principle in Zsigmondy's ultramicroscope. There are, of course, other types of ultra-microscopes in use.

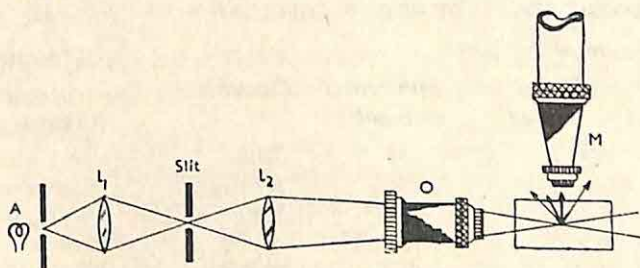


FIG. XVI.3 Ultra-microscope (Zsigmondy)

XVI.5. Electrical Properties of Lyophobic sols. The electrical properties of lyophobic sols are studied from their behaviour (a) towards added electrolytes and (b) in applied electric fields. These two are closely interrelated and a proper understanding of their behaviour also leads to an explanation of the fundamental question of the stability of the sols.

XVI.5a. Effect of addition of electrolytes to lyophobic sols. It has been stated earlier that while purifying a sol by dialysis the system should not be completely freed from all foreign ions. The presence of small traces of suitable ions is necessary to impart stability to the sol. If the system be divested of all ions, the colloid particles grow bigger and are ultimately thrown out as precipitates.

While small amounts of specific foreign ions are essential, the addition of comparatively larger amounts of a neutral electrolyte proves destructive to the stability of the sol. For example, a small quantity of NaNO_3 solution, when added to, say, 10 c.c. of a dialysed AgI -sol, will cause the colloidal silver iodide particles to precipitate out as a flocculant gelatinous mass, often called *coagulum*, leaving a clear supernatant liquid. This phenomenon of coagulating the sol particles is known as "*flocculation*". If insufficient sodium nitrate be added, either no flocculation or partial flocculation will occur. Such coagulation is found with other lyophobic sols also.

Experimental observations on the coagulation of various sols with different electrolytes led to two general conclusions :

- (i) Ions carrying the charge opposite to that of the colloid particles are effective in inducing coagulation.
- (ii) The larger the valency of the coagulating ion, the smaller is the quantity of electrolyte (containing that ion) necessary to flocculate a given amount of sol in a given time.

These generalisations are often mentioned as *Hardy-Schulze rule*. There may be some exceptions to rule (ii) above where conspicuous adsorbability of the coagulating ion may violate the principle.

Continuing with our example of silver iodide sol, it can be coagulated by, say, NaNO_3 , $\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{Th}(\text{NO}_3)_4$. Silver iodide sol has negatively charged dispersed particles. So the positive ions Na^+ , Ba^{++} etc. are the coagulating ions. This is established from the fact that if NO_3^- ion were responsible for flocculation, then the minimum molar concentrations of the different electrolytes used in equal volumes to coagulate a definite amount of sol completely in just a given time would have been in the ratio 4 : 3 : 2 : 1. But experimentally it is found that the concentrations of ions of higher valency needed is much less than this. Thus if x c.c. of 0.001 M NaNO_3 is required, then x c.c. of 0.0001 M $\text{Ba}(\text{NO}_3)_2$ solution would be quite sufficient for the same coagulation. This proves that oppositely charged ions are responsible for coagulating the dispersed phase and that equicoagulating concentrations of these ions decrease as the valencies increase. On the other hand, if the dispersed particles are positively charged as in ferric oxide sol, the anions would be responsible for coagulation and the equicoagulating concentrations of anions (added in equal volumes) would decrease with increase in their valencies. Some data are quoted below from the literature in respect of As_2S_3 (negative) sol and Fe_2O_3 (positive) sol.

TABLE : EFFECTS OF IONS ON COAGULATION OF LYOPHOBIC SOLS
 As_2S_3 (negative) Sol

Electrolyte	Cation valence	Min. conc. millimoles	Electrolyte	Anion valence	Min. conc. millimoles
NaCl	1	51	KCl	1	103
KCl	1	50	KNO_3	1	131
KNO_3	1	50	KBr	1	138
LiCl	1	58			
KCl	1	30	K_2CrO_4	2	0.325
$\frac{1}{2}\text{H}_2\text{SO}_4$	1	31	K_2SO_4	2	0.219
			$\text{K}_2\text{C}_2\text{O}_4$	2	0.238
CaCl_2	2	0.65	$\text{K}_3\text{Fe}(\text{CN})_6$	3	0.096
BaCl_2	2	0.69			
SrCl_2	2	0.63			
ZnCl_2	2	0.68			
$(\text{UO}_2)(\text{NO}_3)_2$	2	0.64			
MgCl_2	2	0.72			
AlCl_3	3	0.093			
$\frac{1}{3}\text{Al}_2(\text{SO}_4)_3$	3	0.096			

From an examination of series of such experimental results, Schulze and Hardy framed an empirical rule correlating the equicoagulating concentrations of the different ions with their valences. This relation is

$$C_3 : C_2 : C_1 = 1 : 11.5 : 730 \quad \dots (A)$$

where C_1 , C_2 and C_3 are the concentrations of mono, bi and tervalent coagulating ions.

It was realised quite early that the coagulation is effected through the adsorption of oppositely charged ions. Then an approximate attempt to explain Schulze-Hardy rule assuming that charges of the particles are counterbalanced by adsorption was made: Applying Freundlich adsorption isotherm, and assuming that all ions are adsorbed to the same extent, we may write

$$x/m = kC^n$$

and electrically equivalent amounts of ions of different valencies are $C_3 : C_2 : C_1 = 1 : 1.5 : 3$. Therefore, amounts adsorbed are in the ratio

$$kC_3^n : kC_2^n : kC_1^n$$

or

$$C_3 : C_2 : C_1 = 1^n : (1.5)^n : 3^n$$

If $n = 6$, an appropriate value, then $C_3 : C_2 : C_1 = 1 : 11.4 : 729$.

The Schulze-Hardy rule is only approximately correct. Although it has been corroborated in ample number of instances there are many contradictions also from experimental standpoint. Specific ion character sometimes comes into play and upsets valency rule. Capillary active or highly adsorbable ions, especially H^+ or OH^- ions, have coagulating capabilities much higher than those of other monovalent ions.

A theoretical relation, derived recently by Verwey and Overbeek, can be used to compute the effect of different electrolytes on the coagulation of a sol. The relation is

$$\left[\frac{1}{v_+} e^{2v_+} + \frac{1}{v_-} e^{-2v_-} - \frac{v_+ + v_-}{v_+ v_-} \right] C = \text{constant}$$

where C = conc. of the coagulating electrolyte : v_+ , v_- are the numbers of positive and negative ions formed from an electrolyte molecule.

XVI.5b. Effect of applied electric field on lyophobic sols. If two electrodes are inserted in a lyophobic sol (Fig. XVI.4a) the disperse phase migrates slowly either to the cathode or to the anode. This indicates that the colloid particles are charged either positively or negatively. In fact, the flocculation of lyophobic sols by addition of electrolytes also suggested the same. The migration of the colloidal dispersed particles in electric field is called *electrophoresis* or sometimes, though not happily, *cataphoresis*.

On the other hand, if the sol is enclosed by compact diaphragms, so that the motion of the sol particles be mechanically prevented and the two electrodes are inserted in the dispersion medium outside the diaphragm (Fig. XVI.4b), then the dispersion medium moves through the diaphragm towards one of the electrodes. This relative motion of the dispersion medium in the electric field is known as *electroosmosis* or *endosmosis*.

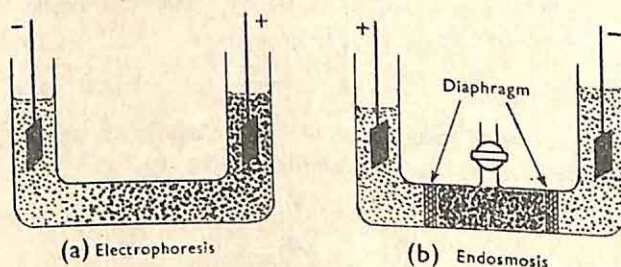


FIG. XVI.4

Both electrophoresis and electroosmosis observed with colloidal systems are just the specific illustrations of the general interface phenomena, namely the electrokinetic effects. These therefore can be explained in terms of the electrical double layer theory as before (vide chapter 14, section XIV.9 et seq.) In colloidal systems, due to smallness of sizes of sol particles, a very large surface area exists. Because of this, the adsorption is very pronounced and the resultant electrokinetic phenomena are conspicuously displayed. Surrounding the charged sol particles, there exist double layers trailed by diffuse layers with their zeta-potentials. The zeta-potentials play an important role in the stability of colloidal state and it is necessary to determine them. The experimental determination of zeta-potential of sols is done either by electrophoresis or by endosmosis. There are different ways of carrying out the two techniques, we shall discuss here briefly one for each.

XVI.5c. Determination of Zeta-potential by Electrophoresis. The evaluation of zeta-potential can be carried out with the help of a micro-electrophoretic cell (Fig. XVI.5). It consists of a flat rectangular glass cell A with a very small (1 mm to 2 mm) but uniform depth throughout. At

the two opposite ends, the cell *A* is prolonged into two cylindrical tubes *B* and *C*, which terminate into two vertical tubes *D*, *D'* and two outlets *E*, *E'*. Two double-way stop cocks *F*, *F'*, one at each end, permit any liquid or sol in *A*, *B* and *C* to be put in communication with either the vertical tubes *D*, *D'* or exit tubes *E*, *E'*.

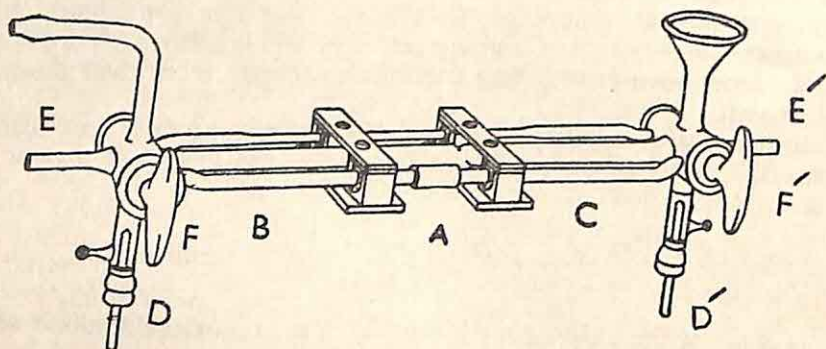


FIG. XVI.5 Micro-electrophoretic cell

To start with a small amount of gelatine sol, made conducting with a little KCl , is poured in *D* and *D'* and allowed to form a gel. The micro-electrophoretic cell is then filled up (*B*, *A* and *C*) with the sol by manipulating the stop cocks *F*, *F'* and allowing outlet *E'* as inlet and sucking through *E*. The sol is next put in communication with the gel in *D*, *D'* by turning the stopcocks. The cell is now placed under a powerful microscope with *A* directly under its objective. The sol particles in *A* at a particular level (0.21 depth of the total to avoid counter streaming) are focussed. A stabilised D.C. field (about 300 volts) is applied through two copper wires dipping in CuSO_4 solutions which rest on the gels in *D*, *D'*. A suitable resistance, a sensitive milliammeter, a commutator are included in the circuit. The sol particles are found to move towards one or the other electrode depending on the charge they carry. The rate of motion of the particles is read off from a previously calibrated scale within the eyepiece.

Now remembering the relation between electrophoretic mobility and ζ , zeta-potential (section XIV.9, equation XIV.10), we can write, for electrophoretic mobility (U/E), as

$$\frac{U}{E} = \frac{\zeta D}{4\pi\eta}.$$

Substitution of E in terms of specific conductivity k of the sol, the current i in amperes, and a , the cross-section of the cell *A*, we have the familiar expression,

$$\zeta = \frac{4\pi\eta U k a}{D i} \times (300)^2 \text{ (volts)}$$

The effect on ζ -potential of adding increasing amounts of neutral electrolyte to the sol can be ascertained similarly. But the amount of electrolyte added should not be large enough to partially or fully coagulate the sol. In the latter case, endosmotic method is to be employed. The micro-electrophoretic method described here is suitable for sols in which the particle sizes are 0.5μ or more, so as to be visible under the microscope. When the sol particles are smaller either micro-electrophoresis with ultramicroscopic arrangement is used or alternative methods involving movement of sol boundary are adopted. The ζ -potentials of emulsions are determined by micro-electrophoretic technique only.

XVI.5d. Determination of Zeta-potential by electroosmotic method. A sketch of the apparatus used in this method is given in Fig. XVI.6. The coagulum formed by the addition of a neutral electrolyte to a sol is transferred to a U-shaped tube provided with two short side arms. It is then centrifuged to form a compact diaphragm filling the entire bottom and a little way up each of the two limbs of the U-tube. The two side-arms are connected through pressure tubings to a rectangularly bent glass tube of uniform cross-section. The portion of the U-tube above the diaphragm, the side arms, the rectangular glass tube, all are filled up with the supernatant liquid obtained during the formation of coagulum from the sol. The continuity of the liquid in the rectangular tube is broken by incorporating an air bubble at the middle of the tube. A stable D.C. field is

applied to the system through two Pt-black electrodes inserted in the two limbs of the U-tube. The circuit as usual includes a milliammeter, an adjustable resistance and a commutator. As electro-osmotic flow of liquid occurs through the diaphragm, the air bubble slowly moves in the tube. The rate of flow of the bubble enables one to calculate the volume rate of flow of liquid through the diaphragm. The ζ -potential may be calculated from the relation, already cited earlier,

$$\zeta = \frac{4\pi\eta kV}{Di} \cdot (300)^2 \text{ volts}$$

The direction of flow of the bubble indicates the nature of the charge of the diaphragm formed by the coagulum.

The complete nature of variation of ζ -potential of a sol with increasing concentration of an added electrolyte can be ascertained by combining the two techniques—*viz.*, electrophoresis and electroosmosis. It is generally observed that the absolute magnitude of ζ -potential goes on decreasing with increase in the concentration of the added electrolyte. In certain instances, as evidenced by electroosmosis, there is even a reversal of sign of ζ -potential implying a change in the nature of charge carried by the coagulum.

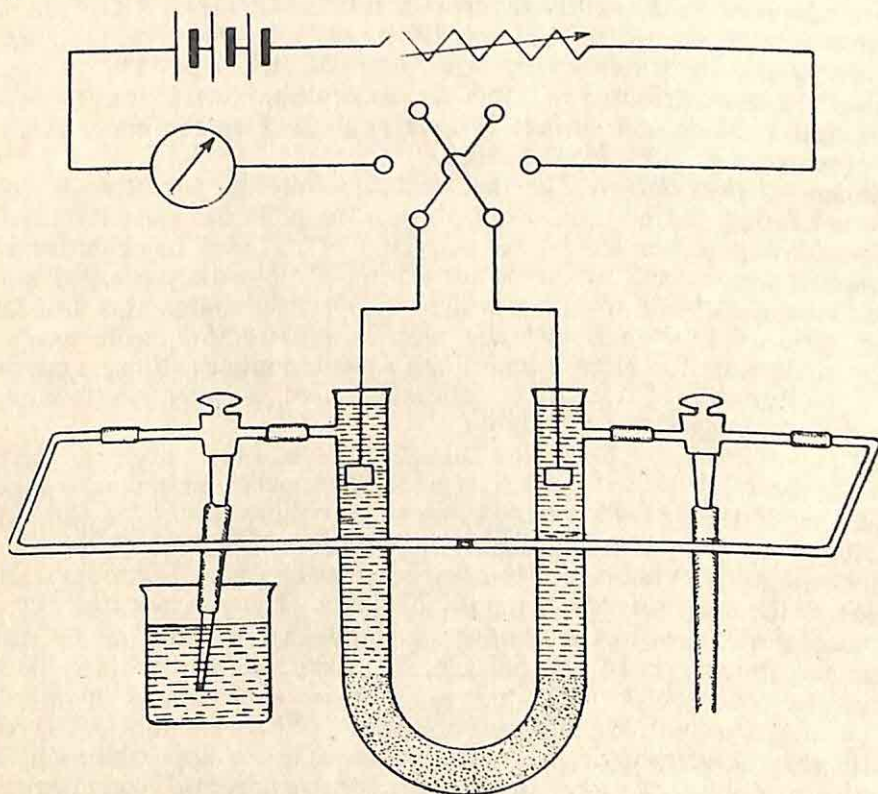


FIG. XVI.6 Electro-osmotic method for determination of ζ .

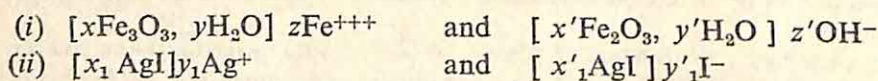
XVI.5e. Origin of charge and the mechanism of flocculation: Theories of stability of sols. The conspicuous effect of ions of particular charge type on the coagulation of sol and the latter's behaviour in applied electric field are indicative of the presence of charges on the surface of the colloidal units. The way of acquirement of these charges is mainly by adsorption and, sometimes, by self-dissociation. Structurally a colloidal unit may be viewed as an aggregate of thousands or tens of thousands of molecules forming a sort of microcrystal. These microcrystals have enormous surface area and hence pronounced adsorption characteristics. They adsorb ions, either positive or negative, from the environmental medium in which they are prepared. Often they exhibit a preference for those ions which are common with one of the ions composing the colloidal microcrystal.

Thus, the colloidal particles of Fe_2O_3 sol, in its preparation from hydrolysis of FeCl_3 by hot water, adsorb Fe^{+++} ions and acquire a positive charge. Fe^{+++} ions are common to both microcrystals and medium. But when Fe_2O_3 sol is prepared from FeCl_3 soln with excess of caustic soda solution, the sol particles adsorb OH^-

ions and become negatively charged, the hydroxyl ions being common to the medium and the hydrated colloidal particles of Fe_2O_3 .

To cite another common instance, the colloidal silver iodide particles have a negative charge due to adsorption of I^- ions when excess potassium iodide is used in its preparation. But if in its preparation excess AgNO_3 is used, the resulting sol particles carry a positive charge due to adsorption of Ag^+ ions.

The structures of the colloidal units of positively and negatively charged Fe_2O_3 sols, AgI sols, may be expressed as :



The preference for common ion adsorption stems from the fact that these ions easily fit in the lattice of the microcrystals. Other ions of similar charge or more or less of similar dimensions may also be adsorbed to impart charge to the colloidal particles. While in positively charged Al_2O_3 sols Al^{+++} ions (and some H^+ ions) are adsorbed by the colloidal particles, it is the adsorbed AlO_2^- ion which is responsible for the charge in the negative Al_2O_3 sols. Sulphide sols, such as As_2S_3 sol, are generally stabilised by adsorption of HS^- ions. The charges on metal sol particles are attributed to either the adsorption of OH^- ions from water or the dissociation of certain surface complexes formed on the metal bodies by the action of water, e.g., $[\text{aPt}, \text{bPtO}_2] \text{Pt}(\text{OH})^-$.

Mechanism of flocculation. The fact that the colloidal particles are charged and that ions bearing charge opposite to that of the colloidal particles have pronounced flocculating power led to the adoption of the idea in primitive stages that flocculation was caused by direct adsorption of oppositely charged ions on the surface. This adsorption would neutralise the particle charge and thus favour coagulation. This idea, though partially true in a sense in specific cases, was found to be inadequate for many reasons and soon renounced. Since coagulation is related to the question of stability of colloidal system, we may therefore explain it from the theories suggested for stability.

Critical Potential theory for colloid stability. From our concept of electrical double layer at the solid-liquid interface, it is readily understood that each colloidal particle will have a double layer surrounding it. The solution part of this double layer consists of a fixed and a diffuse portion (Sec. XIV.9). The diffuse portion will predominantly contain ions bearing opposite charges. The same is true of the fixed part of the solution side of the double layer. Thus, in negatively charged As_2S_3 sol, each particle carries a number of stabilising HS^- ion on its surface. In the close neighbourhood of this particle, there exists in the solution side one layer of oppositely charged H^+ ions which are more or less fixed and beyond this is the diffuse portion also with H^+ ions predominance. When two such As_2S_3 colloid particles with their accompanying shrouds of diffuse layers approach each other, there is repulsion of similar charges and the particles are prevented from coalescing.

If now an indifferent electrolyte, say BaCl_2 , be added, Ba^{++} ions will be preferentially adsorbed on the fixed part of the solution side of the double layer. The colloidal particle together with the fixed part of the solution side will now have a resultant surface density (σ) considerably less than before. The consequence will be the release of a number of H^+ ions from the diffuse part of the double layer. These will migrate to the bulk solution effecting a contraction of the diffuse layer thickness and thus lowering the value of the zeta-potential. It follows that, after addition of BaCl_2 , two As_2S_3 colloid particles can approach nearer because of contraction of the diffuse layer thickness. When the contraction of double layer is quite large, there would be a considerable lowering of ζ -potential, the thermal motions then may overcome the electrical effect and cause coagulation.

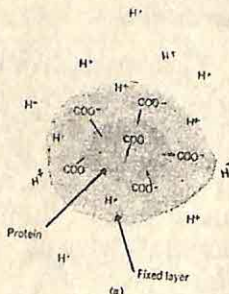


FIG. XVI.7 Colloid particle with fixed and diffuse layers (diagrammatic)

The measurements of zeta-potentials in many sols indicate that when coagulation starts, the ζ -potential values are lowered down to the range 0.02 to 0.05 volts. Ellis and Powis, from a series of experiments, suggested that for a given sol there is a critical value of ζ -potential at which coagulation commences. This is true irrespective of the nature of the electrolytes used for flocculation. Plenty of instances were found supporting the critical zeta-potential theory of colloidal stability. On the other hand, there were cases which contradicted the theory, though in many cases the discrepancies were due to neglect of certain factors in ζ -potential measurements.

Theory of Verwey and Overbeek : A little over two decades ago, a full quantitative theory of the stability of lyophobic sols were put forward by the Dutch chemists Verwey and Overbeek. Similar ideas were also developed independently somewhat earlier by the Russian chemist Derjaguin.

The salient features of the mathematical theory may be qualitatively stated as follows. The diffuse double layers of the colloid particles interact when particles approach each other. This interaction energy depends, among other things, on the inter-particle distance as well as on κ , the reciprocal of the thickness of the ion atmosphere. This interaction energy of the double layer gives the potential energy curve of the two colloid particles and it turns out to be a repulsive potential. Further, Verwey and Overbeek consider the London van der Waals' forces operative between colloidal units. This happens to be an attractive potential. The total potential energy curve could thus be constructed by superposition of both the attractive and repulsive potentials. It is found that for any given particular ionic strength, and hence κ , the attractive potential overshadows the repulsive potential at very short and at very large distances. For intermediate distances between the particles, the repulsive potential is prominent. The addition of electrolyte affects the repulsive potential only and the nearest point where repulsion between the colloid particles gains ascendancy over attraction between them recedes further and further from the particle surface with increasing κ . In this way, a fuller explanation of colloid stability and coagulation has been worked out.

XVI.6. Properties of Lyophilic sols. Certain distinctive features of lyophilic colloidal systems have been mentioned earlier. In general, lyophilic sols show very weak Tyndall scattering and, unlike lyophobic sols, do not coagulate with the addition of small quantities of electrolytes. Considerable quantities of electrolyte solution added to lyophilic systems cause the latter to separate out in clusters or *coacervates*. Generally it is often called "*salting out*". The ability of different cations or of anions in salting out varies from ion to ion ; and the valences of ions concerned also have definite influence in the process of coacervation.

A series, based on experimental observations and called Hofmeister series or *lyotropic-series*, has been drawn up for anions and for cations demonstrating qualitatively their capacity in salting out the lyophilic micelles. The series are

(a) for anions : $\text{Ac} > \text{Cl} > \text{NO}_3 > \text{Br} > \text{I} > \text{CNS}$

(b) for cations : $\text{Th} > \text{Al} > \text{H} > \text{Ba} > \text{Sr} > \text{Ca} > \text{K} > \text{Na} > \text{Li}$ etc.

When two lyophilic systems with opposite charges of the disperse phases are brought together, coacervation occurs. Thus gum and gelatine suspensions having opposite charges when brought together, they are both salted out together in thick micelles. Electrostatic interaction tends to cause coagulation but this is resisted by the elasticity of the water shell surrounding them. The individual charged micelles are held together by electrostatic attraction to form a coacervate.

The principle in *cottrell precipitation* is also similar. Extremely fine dust or solid particles suspended in a gas can be removed by subjecting them to strong electric fields. A high tension current is applied to wires kept hanging in the gas ; the suspended solid particles in the gas become charged. These then recede away from the wires and are deposited at the bottom plates having opposite electrical charge. This method has been profitably applied in purifying gases from dusts, in removing dust of cement plants and of gases from smelters etc.

XVI.6a. Viscosity of Lyophilic sols. A striking difference between lyophobic and lyophilic sols is the high viscosity of the latter. This is due to the extensive solvation of the disperse phases particles which increases the resistance to flow. Einstein deduced an equation for the relative viscosity coefficient of a suspension of

very small rigid spheres in which the radius of the particle r is large compared to the sheath of the medium sticking to each sphere, but much smaller than the average distance of closest approach between any two sol particles. The equation, which is therefore valid for very dilute sol systems, is

$$\eta/\eta_0 = 1 + 2.5\phi = 1 + 2.5 cv$$

where η and η_0 are the viscosity coefficients of the sol and the dispersion medium, and ϕ is the fraction of volume occupied by dispersed phase in a unit ml of suspension. If c gms of sol particles be present per c.c. of the sol and v be the specific volume of the dispersed phase, then $\phi = cv$.

The validity of this relation has been experimentally established in many studies on the viscosities of lyophilic sols, especially with gamboge, mastic, protein sols etc. The independence of the specific viscosity coefficient $\eta_{sp} = \eta/\eta_0$ of a suspension of the particle sizes, for the same ϕ , as demanded by the above relation has been verified in many instances. The discrepancies observed in certain cases are primarily due to the departures from conditions under which the equation is strictly valid.

The numerical coefficient 2.5 is susceptible to changes because it embodies a shape factor. Smoluchowski points out that for rod-shaped particles or for sol particles which are charged the coefficient is increased. The relation proposed is,

$$\eta_{sp} = \eta/\eta_0 = 1 + 2.5 \left[1 + \frac{1}{\lambda\eta_0} \left(\frac{D\zeta}{2\pi r} \right)^2 \right] \phi$$

in which λ is the sp. conductance of the sol, D , dielectric constant, and ζ , the electrokinetic potential. Addition of very small quantities of electrolyte affects the zeta-potentials. It is then expected that in lyophilic sols, the large viscosity values will in general be greatly lowered in presence of small amounts of added electrolyte. This is found to be true for many systems such as sols of starch, gelatine, gum arabic, etc. This pronounced lowering of viscosity in the presence of electrolytes is known as *electroviscous effect*.

XVI.6b. Protective action of lyophilic sols. When lyophilic sols are added to lyophobic sols, the sensitivity of the latter towards electrolytes depends on how and in what manner the lyophilic sol is added. If a little lyophilic sol is added slowly to a lyophobic system the latter becomes very sensitive to flocculation on addition of electrolytes. If however a comparatively large amount is added to a lyophobic sol quickly, the sol becomes more stable and thus less sensitive towards electrolyte addition. Lyophilic sols thus can play a protective role as *peptisers*.

All lyophilic sols do not afford the same degree of protection to any given lyophobic sol. As a measure of their protective capacities Zsigmondy set up a standard by which protective capacities are expressed in terms of what is called '*Gold numbers*.' The weight in milligrams of the disperse phase of the lyophilic sol in the dry condition, which ought to be added to a 10 c.c. portion of a standard Gold sol (appr. $5.5 \times 10^{-3}\%$ by wt.) to just prevent its turning from red to blue on the addition of 1 c.c. of a 10% solution of NaCl, is called the '*gold number*' of the lyophilic sol. The change of colour is indicative of the start of flocculation. It is evident that the lower the gold number the greater is the protective action of a lyophilic colloid. Gelatine, salts of protalbic and lysalbic acids obtained from albumen, etc. have low gold numbers and thus high protective capacities. Some of the gold numbers are given here.

TABLE : GOLD NUMBERS OF LYOPHILIC SOLS

Sol	Gelatine	Haemoglobin	Albumin	Gum-arabic	Dextrin	Potato starch
Gold number	0.005–0.01	0.03–0.07	0.1–0.2	0.15–0.25	6–20	>25

It is not clearly understood how the lyophilic sol affords protection to lyophobic colloidal particles against flocculation but it is obvious that the particles of the two sols are associated or united in some manner.

XVI.6c. Gelation. Lyophilic sols and also some lyophobic sols possessing a good degree of lyophilicity have the property of setting to a semi-solid jelly-like condition, called a *gel* at ordinary temperatures. This happens in lyophilic sols provided these are fairly concentrated. In lyophobic sols gelation depends on two conditions that these are not too dilute and that an amount of foreign electrolyte be present in the sol at certain optimum concentrations. Truly lyophilic sols such as gelatine, agar, gum arabic, protalates, mastic, gamboge etc. all exhibit this gelation property. Of the lyophobic sols having this property, mention may be made of silicic acid sol, ferric phosphate sol etc.

Gels are characterised by (1) high viscosity values and (2) considerable swelling if placed in the dispersion medium, for example, if silicic acid gel or gelatine gel be suspended in water, considerable quantity of water is absorbed by the gel and there is a simultaneous swelling of the gel-body. This phenomenon is known as *imbibition*. The most interesting fact in imbibition is that the sum of the net volume of water absorbed and the volume of the gel absorbing it is more than the total volume of the swollen gel. This implies that the structure of a gel is a three-dimensional net-work with large number of void spaces wherein the sorbed molecules of water (or dispersion medium) are accommodated.

Gels, on standing, give out small quantities of liquid (e.g., water) which accumulate on the surface. This is known as *syneresis*. During syneresis there is no contraction in gel volume which again points to a rigid three-dimensional net work structure in a gel.

Gels are broadly divided into two groups : elastic gels and non-elastic gels. The main difference between the two is in their behaviour upon dehydration and rehydration. Partial dehydration of an elastic gel, say gum, leads to an elastic solid from which the gel can be easily obtained again by addition of water. But a non-elastic gel like silicic acid on dehydration gives a glassy powder and cannot be reconverted into gel by adding the solvent.

Some gels such as ferric phosphate, ferric oxide, gelatine, etc. when subjected to mechanical shaking lose their semi-solid gel character and acquire the behaviour of sols. They again set to a gel on standing. This phenomenon is known as *thixotropy*. Sometimes, thixotropic gels are obtained by adding electrolytes within certain limits to ordinary sols. Vanadium pentoxide, alumina, bentonite clay also constitute some of the examples of this class. When electrolytes are added, the sols flocculate in the form of gel. If too small or too large quantities of electrolytes are added, gelation does not set in and no thixotropic property is observed.

Thixotropy has many important applications. In drilling deep oil wells or tube wells, a drilling fluid has to be used in order to prevent the rock-chips cut by the drill from forming a compact mass. The drilling fluid, such as bentonite suspension keeps the stone chips in suspension in its gel. When the drill is in operation the gel is transformed to a sol. Tooth pastes and medicinal ointments kept in tubes are in gel states. Under a pressure these flow out more easily with increase in fluidity. Quicksand is an example of thixotropic behaviour. Undisturbed it is in a gel state. When an animal moves on it, it turns into a sol and the animal begins to go down. The more it struggles to come out, more mobile the sol becomes and further the animal sinks.

XVI.7. Kinetic properties of sols : Brownian motion. In the latter part of the nineteenth century Brown, a botanist, observed under a microscope that pollen grains suspended in a liquid had a ceaseless chaotic and haphazard movement. Sol particles when examined under a microscope or an ultra-microscope (through Tyndall scattering) are also found to execute random zigzag ceaseless motions. Such movements are called *Brownian motions*. Even when all possible causes which may lead to motions, such as heat, light, mechanical vibrations and other possible disturbances are carefully eliminated, the particles move about ceaselessly for months and months. It is therefore concluded that Brownian motions are due to molecular impacts from the medium on all sides of these dispersed particles. That the Brownian motion becomes less and less vigorous with the increase in the dimensions of the suspended particles of the sol, as also with the increase in the viscosity of the medium are in conformity with the collision theory proposed.

The existence of Brownian motion is an indirect evidence of the existence of molecules and of thermal motion performed by molecules. It also additionally demonstrates that at any instant the numerous impacts suffered by a sol particle on all sides are not evenly matched and this results in a net displacement in a macroscopic time element. There is, however, no preference for directions in these displacements.

One may draw certain analogies between the kinetic behaviour of the sol particles in a colloidal system and that of the solute particles in an ideal solution. The ideal gas laws are obeyed by dilute solutions which suggest that the solute particles undergo chaotic movement similar to those of the gas molecules. The only restriction for the validity of the gas laws in solution is that the solution must be dilute; size of the solute molecules, big or small, makes no difference. If, therefore, we consider solute particles to be so big as can be identified with the kinetic units of a colloidal system, we should expect the kinetic theory considerations to apply to such systems.

The idea of such an applicability of kinetic theory to sols enables one to determine an important physical constant, N_0 , Avogadro's number, from a study of Brownian motion in a suspension. The principles of two such methods for the determination of Avogadro's constant are described here.

XVI.8. Determination of Avogadro's Number from Vertical distribution of Sol particles. Consider a dilute suspension contained in a tall cylinder. The equilibrium distribution of the sol particles at different heights from the bottom of the container will depend upon the forces acting on the particles. Had the gravity force only been operative, all the sol particles would settle down to the bottom after a time. But the sol particles undergo Brownian motions which have no preference for directions. Take a sol particle at a height h_0 from the bottom and let it undertake certain Brownian displacements in diverse arbitrary directions. The projection of the resultant displacement on the vertical axis will measure the vertical displacement, either upward or downward, of the particle from the reference plane at h_0 . It is evident that in the case of downward displacement it aids the gravity force and in the opposite event, the Brownian displacement acts against gravity settling.

The situation is quite analogous to the distribution of pressure and, hence, of molecules of a gas contained in a tall vertical column. The distribution of the gas molecules at different heights is obtained in the following way.

Let the pressure at height, h_0 (reference plane) $= p_0$
and the pressure at height, $h_0 + dh_0 = p_0 - dp_0$

The downward thrust of the gas due to the column between h_0 and $h_0 + dh_0$ heights is counterbalanced at equilibrium by the upward thrust (F_0) of the said portion originating from the kinetic motions of the gas molecules.

If σ be the cross-section of the column and ρ_0 the density at height h_0 , then

$$\sigma \rho_0 g dh_0 = F_0$$

or

$$\sigma \rho_0 g dh_0 = -dp_0 \cdot \sigma \quad \dots (A)$$

The upward thrust F_0 is equal to $|dp_0 \sigma|$, the negative sign in (A) is due to the fact that dp_0 denotes increment of pressure.

Again, from kinetic theory.

$$dp_0 = \frac{1}{3} mc^2 dn_0 = \frac{2}{3} \cdot \frac{1}{2} mc^2 \cdot dn_0 \quad \dots (B)$$

where n_0 is the number density of the molecules at height h_0 . Substituting $\frac{1}{2} mc^2$ by $3/2 kT$ per molecule, k being Boltzmann constant, we have

$$dp_0 = kT dn_0$$

On introducing this in equation (A),

$$mn_0 \cdot g \cdot dh_0 = -kT dn_0 \quad (\because mn_0 = \rho_0)$$

or

$$kT \frac{dn_0}{n_0} = -mg dh_0 \quad \dots (C)$$

Integrating (C) over a height h_1 to h_2 with the corresponding number densities n_1 and n_2 , we have (Fig. XV.8)

$$kT \ln \frac{n_1}{n_2} = mg(h_2 - h_1) = mg \Delta h$$

Since $k = R/N_0$,
$$\frac{RT}{N_0} \ln \frac{n_1}{n_2} = mg \Delta h$$

i.e., Avogadro's number, $N_0 = \frac{RT \ln n_1/n_2}{mg \Delta h} \dots (D)$

This relation (D) valid for distribution of molecules in a gas will also hold good for equilibrium distribution of sol particles in suspension. For a homogeneous suspension with spherical sol particles of radius r and with effective density $(d-d_0)$, since the particles are suspended in a medium of density d_0 , equation (D) may be written as,

$$N_0 = \frac{RT \ln n_1/n_2}{\frac{4}{3}\pi r^3 (d-d_0) g \Delta h} \dots (XVI.1)$$

The determination of N_0 , therefore, demands the experimental measurements of the following quantities :

- n_1 and n_2 or n_1/n_2 at heights h_1 and h_2 ,
- $(d-d_0)$, the effective density of the sol particles,
- the radius r of the sol particles.

In a series of painstaking and laborious investigations Perrin and, afterwards, other investigators determined the quantities involved in equation (XVI.1) and evaluated N_0 . The methods followed for such determinations are very briefly narrated below. The experiments were made with a dilute and as far as possible homogeneous suspension of gamboge. The sol was allowed to stand in a cylinder to attain distribution equilibrium.

(a) *Determination of n_1, n_2 and Δh* : To determine (n) number of particles at a level, a powerful microscope with a disc having a central hole fixed in the focal plane was used for counting n_1, n_2 etc. The microscope was focussed for a view of the level at height h_1 . The presence of the small hole in the disc severely delimited the area of vision and there flashed only a few of colloidal particles at any instant, in the visible area. An instantaneous impression (not exact) counting of the number was recorded. Since the sol particles were constantly moving about, the number in the visible area did not remain constant. A very large number (200 or 300) impression countings were made. The microscope was next focussed on to a different level, h_2 , and the difference in the two levels (Δh) was read off from the vertical scale of the microscope. At this new level also, an equal number of impression countings were made. The ratio of the totalities of the two series of impression countings gave the value of n_1/n_2 .

(b) *Determination of density* : The density of the sol (d') and that of the medium (d_0) were independently determined in the usual way using pycnometers. Next, a definite weight (w') of the suspension was evaporated to dryness and the weight of the solid residue (w) was found out. The weight of solvent present in w' weight of sol would then be $w' - w$. Assuming no change in volume due to sol formation, we may write

$$\frac{w'}{d'} = \frac{w' - w}{d_0} + \frac{w}{d}$$

from which d , the density of sol particles was known. The effective density $(d-d_0)$ was thus obtained.

(c) *Determination of ' r '* : A quantity of the suspension was shaken and then allowed to settle in a tall column. The particles, in the course of settling under equilibrium conditions, acquired a steady velocity of fall ' u ' especially at the early stages. The velocity of fall was ascertained by

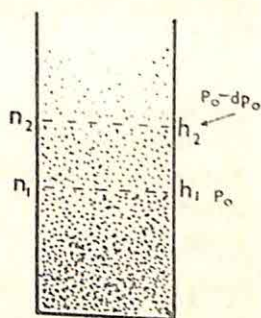


FIG. XVI.8
Vertical distribution
of particles

noting the time required by the particle to move vertically down between two fixed lines with a stop watch, observing through a microscope. Stoke's relation,

$$6\pi r\eta u = 4/3\pi r^2(d-d_0)g$$

was then used to determine 'r'.

Other methods were also employed to obtain the density and radius of suspended particles. The results obtained from different methods were practically the same. Avogadro's number determined by Perrin and others in this way using different sol systems was found to be roughly in the range $6.2 \sim 7.0 \times 10^{23}$.

XVI.9. Determination of Avogadro's number by Diffusion method. In a suspension, the particles execute haphazard movement continuously in all directions. It is however possible to consider the displacements only in one direction. The displacements of a single particle in a given time interval τ when projected on a plane may be imagined as shown in Fig. XVI.9. The same particle will have different displacements in successive equal intervals of time. Different particles in any given τ must also be different. As movements in all directions are equally probable, without any preference for a particular direction, it may be reasonably supposed that half the particles would have displacements along the positive and the other half along the negative direction of the axis. Einstein (1905) first derived a relation between such displacement, parallel to the horizontal x -axis, of the sol particles and the Avogadro's number, N_0 .

Consider a portion $PQRS$ of a cylinder of cross-section ' σ ' placed horizontally and containing a suspension with concentration gradually decreasing from left to right (Fig. XVI.10). Let MN be an imaginary plane at a distance x from either PQ or RS and let n_1 and n_2 be the average number densities of sol particles in chambers PN and SN respectively, ($n_1 > n_2$). Then n_1 and n_2 may be taken to represent the actual number densities at the planes aa' and bb' at the middle of the two chambers. The concentration gradient of the sol particles would then be,

$$-\frac{dn}{dx} = \frac{n_1 - n_2}{x}, \quad \dots (i)$$

the negative sign is given as the conc. n decreases with positive direction of x .

The diffusion of particles from the concentrated to the dilute region across MN will depend on the horizontal components of the brownian motion of the sol particles on either side of MN . Whatever be its net brownian displacement in a definite time τ , it will have a net horizontal displacement (Fig. XVI.9).

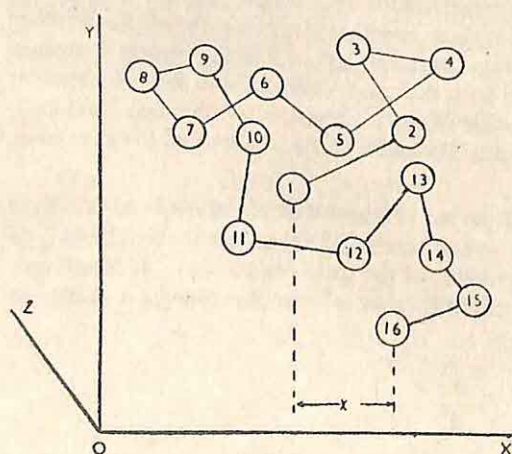


FIG. XVI.9

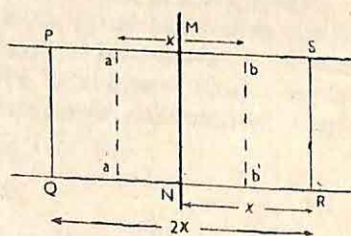


FIG. XVI.10

Let the average value of such horizontal displacement components of the particles be x in time τ . Since brownian motions can occur in all directions with equal probability, we can assume that half the total number of particles in PN

have a net horizontal displacement towards left and the other half to the right. The latter half diffuses through MN . Similarly for the chamber SN , half the total number would have net horizontal translations towards left and would diffuse through MN into chamber PN .

Thus, the number of sol particles passing across MN in time τ from the chamber PN to $SN = \frac{x\sigma n_1}{2}$; and the number passing from SN to $PN = \frac{x\sigma n_2}{2}$.

Hence net diffusion across MN in time $\tau = \frac{1}{2}x\sigma(n_1 - n_2)$. . . (ii)

Now the quantity of the substance (Q) which diffuses through a given cross-section σ (taken at rt. angles to the direction of diffusion) per second is directly proportional to the cross section and to the concentration gradient along this direction, $-dn/dx$. Hence,

$$Q = -D\sigma \left(\frac{dn}{dx} \right) \cdot \tau$$

where the constant of proportionality D is called the diffusion coefficient.

In the previous case, the quantity diffusing in time τ is given by equation (ii). Therefore, we can write

$$-D\sigma \left(\frac{dn}{dx} \right) \cdot \tau = \frac{1}{2}x\sigma(n_1 - n_2)$$

Substituting from (i), $D\sigma \frac{(n_1 - n_2)}{x} \tau = \frac{1}{2}x\sigma(n_1 - n_2)$

$$\text{or} \quad D = \frac{x^2}{2\tau} \quad \dots (iii)$$

Assuming that ideal solution laws are applicable to homogenised suspensions as well, we may represent osmotic pressures at any point in the planes aa' and bb' as

$$p_1 = 1/3 mn_1c^2; \quad p_2 = 1/3 mn_2c^2$$

[c^2 = mean square velocity of suspended sol particles and m the mass of each particle]. The difference of pressures is

$$\Delta p = 1/3 mc^2 (n_1 - n_2)$$

i.e., the osmotic force difference, $\Delta p\sigma = 1/3 mc^2 (n_1 - n_2)\sigma$

This osmotic force difference is responsible for the net diffusion as given in equation (ii) across MN in time τ .

The net osmotic force (f) acting on each particle diffusing in time τ (with an average velocity x/τ , x being displacement in time τ), is given by,

$$f = \frac{\Delta p\sigma}{\frac{1}{2}x\sigma(n_1 - n_2)} = \frac{\frac{1}{3}mc^2(n_1 - n_2)\sigma}{\frac{1}{2}x\sigma(n_1 - n_2)} = \frac{1}{3}mc^2 \cdot \frac{2}{x} \quad \dots (iv)$$

Now the mean square velocity, $c^2 = \frac{3RT}{M} = \frac{3RT}{mN_0}$, where N_0 is Avogadro's number. Therefore, equation (iv) can be written as the driving force on a single particle diffusing, with velocity $\frac{x}{\tau}$, i.e.,

$$f = \frac{RT}{N_0} \cdot \frac{2}{x} \quad \dots (v)$$

Under steady condition, this driving force should be equal to the opposing viscous force. Hence, from Stoke's law and equation (v), we have,

$$\frac{RT}{N_0} \cdot \frac{2}{x} = 6\pi\eta r \frac{x}{\tau} \quad \dots (vi)$$

$$\text{from which,} \quad N_0 = RT \cdot \frac{1}{3\pi\eta r} \cdot \frac{\tau}{x^2} \quad \dots (vii)$$

$$\text{or, using (iii),} \quad N_0 = \frac{RT}{D} \cdot \frac{1}{6\pi\eta r} \quad \dots (vii.a)$$

This relation was used to determine Avogadro's number, N_0 .

It may be noted that although the relation (vii) has been developed assuming concentration gradient, it does not contain n_1 or n_2 , i.e., independent of conc. gradient. The brownian displacement x , depending only on the impact of the medium molecules, is independent of uniform or non-uniform arrangement of the sol particles in the dispersion medium.

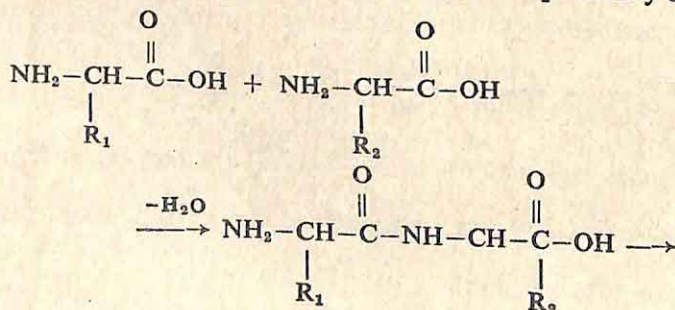
It is seen that for determining N_0 , it would be necessary to find out experimentally η , r and x^2 (in a time τ). The viscosity η is determined in the usual way, and the method for ' r ' the radius has already been described in the previous section.

The mean square displacement x^2 was determined by Perrin for homogeneous gamboge and other suspensions in the following way. The particles of a suspension were focussed under a microscope. The latter carried within its eye-piece the design of a square paper, the length of each small square of which was previously calibrated. The translational brownian displacement along the x -axis was read off by noting its position on the square design within the eye-piece. Perrin made a large number of observations on a single particle, noting its horizontal displacement at every 30 seconds interval. This was repeated for a large number of particles. The magnitude of x^2 in time τ ($= 30$ secs) was thus determined.

A brief summary of other methods employed for the determination of N_0 is given in appendix VI.

XVI.10. Macromolecules. The characteristic behaviour of sols is exhibited when the particle size of the dispersed phase ranges between $100 \text{ \AA}$ and $10000 \text{ \AA}$. There are many molecules which are large enough to be in the range of colloidal dimensions. Their molecular weights are quite high ranging from, say 5000 to one-million or so. These are really giant molecules, now-a-days mentioned as *Macromolecules*. Examples of macromolecules occurring in nature are those of proteins (gelatine), nucleic acids (*DNA*), polysaccharides (cellulose), polyisoprenes (natural rubber), etc. On the other hand, through polymerisation reactions, molecules of low mol. wt. join up through primary valences into large giant ones by repetitive manner. Thus, ethylene ($M = 28$) polymerises to give polyethylene of mol. wt. more than 30000. In natural macromolecules also, as in proteins, a large number of similar structural units are joined together by the same kind of linkage. To illustrate, some basic reactions may be cited.

The formation of protein from amino acids is primarily based on a reaction as,

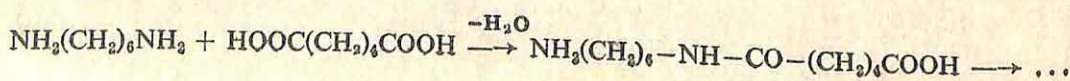


This goes on repeating until a giant-size molecule is formed.

In synthetic polymers, polyethylene is synthesised from ethylene units as,

$$[-\text{CH}_2\text{---CH}_2\text{---}]_n \longrightarrow [-\text{CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---}\dots]$$

The synthesis of nylon from hexamethylene diamine and adipic acid is achieved through the repetition of



The shape of the macromolecules also varies, some of them are nearly spheroidal, some of them are rod-like, again many of these have coiled chains repeatedly folded. When there are cross-linkings between the units or chains, the macromolecules become rigid which makes them infusible and insoluble materials, such as bakelite, vulcanised rubber etc. The physical character of macromolecules primarily depends on their shape and size.

XVI.11. Properties of Macromolecular solutions : Viscosity. Many of the macromolecular substances dissolve in suitable solvents to form true solutions just like sugar or urea dissolving in water. Dilute solutions of ordinary substances, we know, obey the 'ideal' laws. These solutions are governed by thermodynamically based relations in respect of their boiling points, osmotic pressure, freezing points etc. (Chapter XI). But the great disparity in size and shape of the macromolecules and ordinary molecules is responsible for the departure from ideal laws in the behaviour of the solutions of the former even at very low concentrations.

In fact, the solutions of macromolecules or polymers behave like lyophilic sols, the solutes having sizes in the colloidal range. There is often considerable interaction between the solute (macromolecules) and the solvent. The macromolecular solutions exhibit high viscosities at quite low concentrations. This increase in viscosity on addition of polymer solute to a solvent may be quite enormous. It may be caused by very extensive solvation of the solute molecule which immobilises the bound liquid, or the unusually long polymer molecules may be intertangling with each other as they move. In fact in many of the polymers is observed a strong propensity of the solvent-free materials to *imbibe* the solvent. Gelatine in water, rubber in benzene, cellulose in water, etc. are common examples in which considerable swelling occurs on imbibition.

Macromolecules are often precipitated from solution by adding to the solution a solvent in which the polymer is insoluble. During such precipitation, the largest molecules come out first; the lighter molecules follow in order of decreasing molecular weight. This helps also to separate, from a polymer sample, fractions having different mol. wts. of narrow ranges.

The studies in viscosity of polymer solutions also give an opportunity to find out the molecular weight. Some semi-empirical relations have been derived between the individual polymer molecule and the intrinsic viscosity $[\eta]$ of the solution. The intrinsic viscosity is defined as

$$[\eta] = \left[\frac{1}{C} \cdot \frac{\eta - \eta_0}{\eta_0} \right]_{\text{Lt}_{C \rightarrow 0}}$$

where, η is the viscosity of the solution, and η_0 of the solvent. Remembering that a polymer sample is composed of different mol. wt. fractions, the intrinsic viscosity is found to be related to the molecular weight (M) of a fraction as

$$[\eta] = KM^a \quad \dots \text{(XVI.2)}$$

or

$$\log [\eta] = a \log M + \log K$$

the constants K and a are empirical constants depending on the solvent, polymer (size, shape etc.) and the temperature. The experimental determination of $[\eta]$ for several known molecular weight fractions of the same polymer allows evaluation of K and a . When K and a are known, the mol. wt. of any batch of the polymer can be easily obtained [see Sec. II.15].

Molecular weights of polymers. It is necessary to define here the average mol. wts of the samples of polymers. The polymers have a range of molecular weights and any determination of size or weight would necessarily involve some sort of an average value. Two kinds of averages are generally computed.

(i) *The number average mol. wt.*, denoted by $\bar{M}_n$, is defined as the weight of the sample divided by the total number of moles (n) present. Thus, if a polymer sample consists of n_1 moles of mol. wt. M_1 , n_2 moles of mol. wt. M_2 , etc. then

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}{n_1 + n_2 + n_3 + \dots} = \frac{\sum n_i M_i}{\sum n_i}$$

Multiplying both numerator and denominator by N_0 , (Avogadro number),

$$\bar{M}_n = \frac{\sum n_i N_0 M_i}{\sum N_0 n_i} = \frac{\sum N_i M_i}{\sum N_i} \quad \dots \text{(XVI.3)}$$

where N_i denotes the number of molecules with molecular wt. M_i .

The number average molecular weight is naturally shifted towards the lower molecular weights. For example, if a sample contains 5 molecules with $M_1 = 500$, and 5 molecules with $M_2 = 50000$, then $\bar{M}_n = 25250$, although 99% of the sample remained in particles of M_2 -weight.

(ii) The weight average molecular weight, denoted by $\bar{M}_w$, depends on the masses m_i of the material present in different molecular weight fractions; so that

$$\bar{M}_w = \frac{\sum m_i M_i}{\sum m_i}$$

i.e.,

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

If C denotes the concentration in gms per unit volume, then $C_i = \sum N_i M_i$; or

$$\bar{M}_w = \frac{\sum C_i M_i}{\sum C_i} = \frac{\sum C_i M_i}{C} \quad \dots \text{(XVI.4)}$$

Suppose a sample contains 20% of polymer $M_1 = 3000$ and 80% $M_2 = 30000$, by weight, then

$$\bar{M}_w = \frac{0.2(3000) + 0.8(30000)}{0.2 + 0.8} = 24600,$$

but

$$\bar{M}_n = \frac{0.2(3000) + 0.08(30000)}{0.2 + 0.08} = 10714$$

XVI.12. Osmotic Pressure. We may next examine the colligative behaviour of polymer solutions, such as freezing pt. depression, boiling pt. elevation, osmotic pressure, etc. The magnitudes of these quantities primarily depend upon the molar concentration. The laws of dilute solutions are obeyed satisfactorily by ordinary solutions up to a concentration of, say, one percent. But considerable deviations are observed with polymer solutions even at a much lower concentration.

Consider a polymer having molecules of size, say, $200 \text{ \AA}$ radius and unit density. Then its mol-wt. is $\frac{4}{3}\pi(2 \times 10^{-6})^3 \times 1 \times 6 \times 10^{23} \approx 2 \times 10^7$.

It is obvious then that even an extremely dilute solution of concentration $0.00001 M$, will contain 20% of the polymer material. As such the solution, though its molarity is very low, is really not physically dilute.

Again if we take a one percent solution of the polymer, then the concentration of the solution in terms of molarity shall be approximately $5 \times 10^{-7} M$. The freezing point depression or boiling point elevation of such a solution, assuming ideal behaviour, will be of the order of $(10^{-6})^\circ\text{C}$, which is not experimentally detectable. That is why these properties are not studied in connection with polymer solutions. It is only the osmotic pressure of dilute polymer solution, though small, which can be experimentally measured.

It has been shown by McMillan and Mayer (1945), that osmotic pressure (π) of a non-electrolyte solution may be represented as

$$\pi = \frac{RT}{M} \cdot c + B c^2 + C c^3 + \dots \quad \dots \text{(XVI.5)}$$

where c is the concentration in gms/litre. B , C , etc. are virial co-efficients. In the

case of ideal dilute solution, the constants would vanish. We can rewrite the above equation as,

$$\frac{\pi}{c} = \frac{RT}{M} + Bc,$$

neglecting higher powers of 'c' in dilute solutions.

The validity of this relation in dilute polymer solutions is established from the fact that

when $\frac{\pi}{c}$ is plotted against c, a straight line is

obtained (Fig. XVI.11). By extrapolating the line to $c \rightarrow 0$, the intercept RT/M is obtained from which the molecular weight is known. In case of polymers, then mol. wt. obtained is the number average ($\bar{M}_n$).

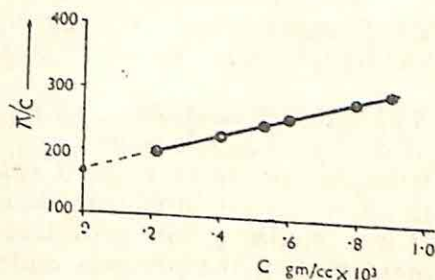


FIG. XVI.11 Osmotic pressure of polystyrene solution in toluene (π in cms of toluene)

Different types of *osmometers* are in use for such studies. One common type consists of a stainless steel chamber fitted with a uniform capillary tube at the top and a swollen cellulose film at the bottom. The steel chamber is filled up with the solution up to the lower end of the capillary. This is then kept immersed in a large container of pure solvent and allowed to attain osmotic equilibrium. The temperature is kept constant throughout.

XVI.12a. The Donnan Equilibrium. It has however been found that even careful measurements of osmotic pressure gave results for mol. wts. of macromolecules much lower than those obtained by other methods. The explanation came from Donnan (1911). In solution, say of a protein, there are giant ions having several units of charges which are counterbalanced by opposite charges of normal sized simple ions. When a protein solution is kept separated from an ordinary salt solution by a semipermeable membrane, it is expected the ordinary ions would only diffuse out, the giant macromolecular ion is indiffusible. But the small ions though diffusible through the membrane do not escape as the energy required to take these away from the field of giant ion is quite high. The observed mol. wt. from osmometric experiment is thus a number average mol. wt. of the giant ion and the other ions dissociated from it. The Donnan's membrane effect would be understood from the following.

Suppose a semipermeable membrane separates a sodium chloride solution (conc. c_1) from a solution of NaP (conc. c_2), in which P^- is a non-diffusible macromolecular ion. Since P^- ions cannot diffuse but Cl^- ions can, the latter will pass from one side to the other. To maintain electrical neutrality, sodium ions will also diffuse. At equilibrium, an amount x of Na^+ and Cl^- ions would pass. The concentrations would be as follows, because of electrical neutrality in each chamber.

	I			II		
	Na^+	Cl^-		Na^+	P^-	Cl^-
Initially :	c_1	c_1		c_2	c_2	0
At eqm :	$c_1 - x$	$c_1 - x$		$c_2 + x$	c_2	x

Since the chemical potential of NaCl will be the same at either side, $\mu_{NaCl I} = \mu_{NaCl II}$

$$\text{Hence } \mu^0 + RT \ln (a_{Na^+ I} \cdot a_{Cl^- I}) = \mu^0 + RT \ln (a_{Na^+ II} \cdot a_{Cl^- II})$$

$$\text{i.e., } a_{Na^+ I} \cdot a_{Cl^- I} = a_{Na^+ II} \cdot a_{Cl^- II}$$

$$\text{Assuming ideal behaviour, } (c_1 - x)(c_1 - x) = (c_2 + x)x, \text{ or } \frac{x}{c_1} = \frac{c_1}{c_2 + 2c_1}$$

i.e., the fraction of NaCl diffused depends on c_2 . If c_2 is large, the amount diffused would be smaller. It gives,

$$x = c_1^2 / (c_2 + 2c_1).$$

The osmotic pressure of the solution is then,

$$\pi = RT\{(c_2 + x + x + c_2) - (c_1 - x) - (c_1 - x)\}$$

$$\text{or} \quad \pi = 2RT(c_2 - c_1 + 2x) = 2RTc_2 \frac{(c_1 + c_2)}{(c_2 + 2c_1)} \quad (\text{substituting } x).$$

The measurements of osmotic pressure in such a condition, *i.e.*, 'swamping out' the Donnan effect by using high concentration of electrolytes, gave satisfactory results for mol. wts. of macromolecules.

XVI.13. Sedimentation : Ultracentrifuge. In Perrin's experiments, the distribution of dispersed particles in a vertical column was considered [Sec. XVI.8]. The distribution, or we may call it *sedimentation*, was under the force of gravity. Unless the particles are large, the sedimentation under gravity occurs at a very slow rate. It was Svedberg who introduced an entirely new technique for studying the sedimentation of the particles under the influence of a field many times greater than gravity. He achieved this with centrifugal sedimentation by rotating the suspension at a very high rate in an *ultracentrifuge*.

The ultracentrifuge is a very high-speed centrifuge in which the sedimentation is effected under an enormous centrifugal force of rotation. The suspension is taken in a specially designed cell and vigorously whirled in special rotors. The speed of rotation is so high that an acceleration as high as million times that of gravity is attained. The use of ultracentrifuge not only hastens the process of sedimentation but it also separates the molecules on the basis of differences in mass, density or shape. The ultracentrifuge proved the most valuable weapon in the study of macromolecular solutions, especially the proteins. Its originator Svedberg was awarded the Nobel prize for its development.

The investigations on the sedimentation in ultracentrifuges of macromolecular solutions are made in two ways. In the first method, called *sedimentation equilibrium*, the sedimentation is allowed to proceed until an equilibrium distribution throughout the cell is reached. It requires a longer time of centrifuging, the concentration of the particles is measured in the ultracentrifuge cell as a function of distance out from the centre of rotation. The concentration is usually obtained from some optical methods of estimation, say refractive index.

Suppose, on attainment of eqm, the concentrations (in gms per c.c.) of the particles at distances x_1 and x_2 from the centre of rotation be c_1 and c_2 , ($x_2 > x_1$). The centrifugal force (f) on a particle of mass m at a distance x is

$$f = m'x\omega^2,$$

where ω is the angular velocity and m' is the effective mass of the particle in suspended state.

If v be the specific volume (*i.e.*, volume of 1 gm) of the solute or suspended material and ρ , the solvent density, then $m' = m(1 - v\rho)$.

Now, the free-energy change involved in moving a particle, from x_1 to x_2 , is

$$\begin{aligned} \Delta G_{cent.} &= - \int_{x_1}^{x_2} m'x\omega^2 \cdot dx = - \int_{x_1}^{x_2} m(1 - v\rho)x\omega^2 dx \\ &= -m(1 - v\rho)\omega^2 \cdot \frac{x_2^2 - x_1^2}{2} \end{aligned}$$

The negative sign is used as free energy decreases with increase in x .

Apart from the centrifugal force acting on the particle, there is also the tendency of diffusion in the opposite direction. The work involved in diffusion for one particle *i.e.*, free energy change is

$$\Delta G_{diffusion} = \frac{RT}{N} \cdot \ln \frac{c_2}{c_1}$$

At eqm, the net $\Delta G = 0$,

$$\text{i.e.,} \quad \frac{RT}{N} \ln \frac{c_2}{c_1} - m(1-\nu\rho)\omega^2 \frac{(x_2^2 - x_1^2)}{2} = 0$$

$$\text{or} \quad M = Nm = \frac{2RT \ln c_2/c_1}{\omega^2(1-\nu\rho)(x_2^2 - x_1^2)} \quad \dots \text{(XVI.6)}$$

As already mentioned that c_2 and c_1 are optically determined, the value of M , mol. wt. of the macromolecule, can be obtained from this relation.

The other alternative is known as the *Sedimentation velocity* method. In this method, starting with a well-defined boundary or layer from near the centre of rotation, its movement towards the outside wall of the cell is carefully followed during very high centrifuging, say 50000 r.p.m. The change in position of the layer is often measured from ultraviolet absorption or from refractive index variation.

The centrifugal force causing the motion of the macromolecules or suspension towards the outer side of the cell is given by

$$f = m(1-\nu\rho)x\omega^2$$

This motion is opposed by the frictional force, given by Stokes equation,

$$f' = 6\pi\eta r \frac{dx}{dt}$$

When the drift-velocity $\frac{dx}{dt}$ is constant, the two forces balance each other,

$$f = f' \text{ i.e.,}$$

$$m(1-\nu\rho)x\omega^2 = 6\pi\eta r \frac{dx}{dt} \quad \dots \text{(A)}$$

Now, the centrifugal field is $x\omega^2$ and the velocity is dx/dt . The velocity under unit field is called sedimentation coefficient(s) and is expressed as

$$s = \frac{dx/dt}{x\omega^2}$$

[Very often the value of s is of the order of 10^{-13} cm/sec per unit field. Sedimentation coefficient unit, has been given the name 'a svedberg' unit equal to 1×10^{-13} cm/sec.]. Rewriting eqn. (A),

$$m(1-\nu\rho) = 6\pi\eta rs$$

$$\text{or} \quad M = N_0 m = \frac{6\pi\eta r N_0 s}{1-\nu\rho} \quad \dots \text{(B)}$$

From equation (vii.a) in section XVI.9,

$$\text{the diffusion coefficient,} \quad D = \frac{RT}{6\pi\eta N_0 r}$$

$$\text{Hence} \quad M = \frac{RTs}{D(1-\nu\rho)} \quad \dots \text{(XVI.7)}$$

The determination of diffusion coefficient, sedimentation coefficient and density permit the evaluation of the mol. wt. of macromolecules.

XVI.14. Scattering of Light. The scattering of a beam of light by a colloidal suspension, giving rise to Tyndall phenomenon, has already been mentioned earlier (Sec. XVI.4). The study with ultramicroscope of the scattered rays revealed the heterogeneous character of the colloid system and also allowed the counting of number of dispersed particles per unit volume. But observation under the ultramicroscope does not furnish any details about the shape and size of the particles. Moreover, if the refractive indices of solvent and suspended particles be not appreciably different, the intensity of the scattered beam is very poor. Measure-

ment and interpretation of the amount of light scattered by a solution of macromolecules in various directions lead to some very interesting results.

When light of wavelength λ and intensity I_0 is passed through a dispersion system of length l and if I be the intensity of scattered light, the relation between I and I_0 is given by

$$\tau = \frac{1}{l} \log \frac{I_0}{I}$$

where τ is the *turbidity* of the dispersion or the colloidal system.

In the case of macromolecular solutions or colloidal suspensions, where the particle sizes are about the same order as the wavelength of the light used, it has been shown by Debye* that the turbidity is related to the concentration by the relation,

$$\frac{Hc}{\tau} = \frac{1}{M} + Bc + Dc^2 + \dots \quad \dots (A)$$

where M is the 'mol. wt.' of the scattering particle ; B , D etc. are constants ; c is the concentration in gms/c.c. The quantity H , which depends upon wavelength of light (λ), the refractive indices, etc., is expressed by

$$H = \frac{32\pi^3 n_0^2}{3\lambda^4 N_0} \left(\frac{n - n_0}{c} \right)^2$$

in which n , n_0 are refractive indices of solution and solvent, N_0 , Avogadro number. Now, for a given solution of known c and n_0 , the turbidity τ and the refractive index n of the solution are carefully measured. The value of H is thus known.

The calculated values of Hc/τ for different solutions are then plotted against c and extrapolated to $c = 0$, from the intercept of which the mol. wt. (M) can be determined with equation (A) above. The mol. wt. so obtained is the 'weight average.'

In measuring turbidity, the emergent beam is generally observed at 90° to the direction of the incident beam. The results are quite satisfactory when scattering particles are small. But in the case of macromolecules, the light scattered from one part of the particle would interfere with that from another part. Hence some correction for dissymmetry of the particle is required. This is obtained from a ratio of scattering intensity at 45° to that at 135° to the incident beam. This ratio is found to be greater than one. Although the experimental difficulties are great yet light scattering has become a very important tool for assessing not only the mol. wt. but also the size and shape of the particles.

XVI.15. Protein Sols. The wide variety of proteins obtained from the living world form the most important group of naturally occurring macromolecules. These are produced from repetitive linking of various aminoacids. As a result the proteins are amphotropic in nature. In solution the protein macromolecules such as gelatine, albumin etc. behave as lyophilic colloids ; they are relatively more viscous and have a tendency to form gels. In an electric field the protein molecules exhibit electrophoretic migration but the direction of this movement depends upon the pH of the medium. In an acid medium, the protein takes up a positive charge and moves towards the cathode, whereas in an alkaline solution the particles would be negatively charged and these would move towards the anode. At a particular H^+ ion concentration in between, the sol would exhibit no movement in an electric field. This is the *isoelectric point* of the sol. The isoelectric point is the pH at which the mobility is zero. The isoelectric points of different proteins are different. Gelatine has the isoelectric point at pH 4.7, indicating that it has no electrophoretic motion at this pH. At a pH above 4.7, it moves towards the anode and at a pH below 4.7, it moves towards the cathode. Similarly, albumin from horse serum has the isoelectric point at 4.9, lecithin at 2.6, etc. The mobility of a protein at a definite

*Debye, J. phys. and colloid chem., 51, 18, (1947). Also read principles of polymer chemistry by Flory pp. 287-90.

pH and ionic strength is a useful identifying characteristic. The way in which the mobility of a protein changes with H^+ ion concentration reveals the nature of the ionisable groups of the protein. Proteins are least soluble at the isoelectric point and have naturally the greatest tendency to 'salt out' at the isoelectric point. In general, the velocities acquired by the particles under unit potential gradient are around 2×10^{-4} cms/sec., which are almost the same as that of simple ions. From the structural standpoint, the proteins are either fibrous or globular. The fibrous proteins, as found in wool, muscle, nail, etc., are insoluble whereas globular proteins, as found in enzymes, egg albumin, haemoglobin, etc., are soluble.

XVI.16. Association Colloids. There are instances where in a solution, with increase in concentration, the solute molecules or their ions come together to aggregate spontaneously to form thermodynamically stable bigger particles of colloidal dimensions. These are called *association colloids* and these usually incorporate into the aggregate appreciable quantity of solvent molecules. The association colloids cannot be regarded as macromolecules as the latter are individual molecules of giant size in solution. They also differ from lyophobic colloids which are thermodynamically unstable. The term '*micelles*' is almost universally employed for the clusters or aggregates formed in solution by association colloids. Although there are some examples of micelle formation from neutral or nonionic molecules, such as polyethylene oxide, but mostly micellizations occur from the large ions of molecules in solution. Usually such molecules have a lyophobic group and a lyophilic group. A typical example of association colloid is that of sodium oleate, $[C_{17}H_{33}]COO^-Na^+$. The long hydrocarbon part $C_{17}H_{33}$ is the lyophobic portion which tries to recede away from the solvent water. But the 'head' $COONa$ is the ionisable lyophilic group which tends to go into water resulting into ions. When the concentration is quite low say less than $3 \times 10^{-3} M$, we have a simple solution of sodium oleate. But as the concentration is increased, the lyophobic hydrocarbon parts receding away from the solvent approach each other and form a cluster as in Fig. XVI.12. The micelle formed is therefore one of anions. The micelle may contain a hundred or more oleate ions clumped together. It is more or less spherical, the hydrocarbon ends are in the interior and $-COO^-$ groups projecting outward, in contact with the solvent. It is thus a colloid particle with charges on the surface to which oppositely charged Na^+ ions would be attracted forming double layers. The name "colloidal electrolyte" is also often used for such suspensions. Similar micellization with anionic groups are found in other soaps, sulphonates, some dyes etc. Micellization with cations are also known as in amine salts such as in CTAB (cetyltrimethyl ammonium bromide), $(C_{16}H_{33})(CH_3)_3N^+Br^-$.

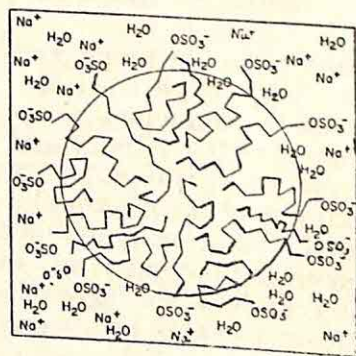


FIG. XVI.12 Micelle formation (diagrammatic)

In very dilute solutions, potassium oleate and similar other substances, which later on micellize, remain as individual molecules ionising into positive and negative ions. Micellization occurs when a particular concentration is reached at a designated temperature. The initial concentration at which micellization begins is designated as the *critical micellization concentration*, abbreviated as cmc. Every association colloid has a definite cmc at a given temperature. Increase of temperature lowers the cmc. The change from ions to micelles is reversible. Hence, by diluting an association colloid, it is possible to revert to the original simple solution.

Starting with a very dilute solution if the concentration is gradually increased, the properties of the solution such as equivalent conductance, surface tension, osmotic coefficient change regularly and smoothly just as with solutions of strong electrolytes. But after reaching a certain concentration, i.e., the cmc, these properties undergo an abrupt change. This is obviously due to the start of the micelle formation. In fact, these properties are observed and

plotted against some function of concentration, say $\sqrt{m}$. From the sudden break of the curve, as shown in Fig. XVI.13, the critical micellization concentration would be known.

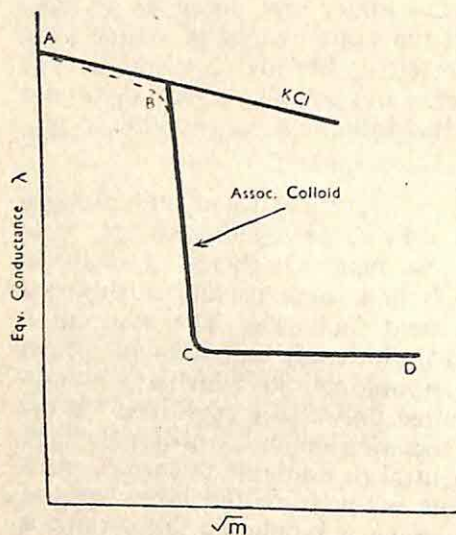


FIG. XVI.13 Eq. conductance of association colloid vs. $\sqrt{m}$

The study of association colloids has become of great importance in recent years as many of these function as excellent detergents and emulsifying agents. These colloids also play a very important part in solubilization of solvent repellant substances by accommodating the latter inside the micelle clusters. Water insoluble dyes are solubilized in soap solutions and subsequently deposited uniformly on fabrics (McBain).

XVI.17. Emulsions. An emulsion is obtained when fine droplets of a liquid are dispersed in another liquid immiscible with it. Milk is a naturally occurring emulsion in which fine globules of fat are dispersed in water. The sizes of the droplets are approximately in the region of 1μ in diameter. Emulsions are often prepared by vigorously shaking together the two liquids, or sometimes these are mechanically

mixed in homogenizers in which one liquid is atomised and sprayed into another. High frequency ultrasonic waves have also been employed in some cases to obtain emulsions. When the emulsions are formed from two pure liquids, their stability is poor and on standing for some time these separate into the two layers of pure liquids. To prepare stable emulsions, it is necessary to add a small amount of an *emulsifying agent*. Soaps of different types, detergents, long chain sulphonic acids, lyophilic colloids such as gelatine, albumin etc. act as emulsifying agents in different cases. In milk, the protein casein serves as the emulsifying agent. The creation of a large number of droplets of a liquid into another liquid increases the surface area and hence requires large amount of energy. The required energy would be less if the surface tension is decreased. The function of the emulsifying agents is to diminish the surface tension.

Emulsions are broadly classified into two types : (i) oil in water type in which the disperse phase is the oil in water medium and (ii) water in oil type in which water droplets are dispersed in oil. Here the term 'oil' is synonymous with any liquid immiscible with water. The type of emulsion produced depends upon the nature of the emulsifying agent used. Thus, when sodium oleate is used as an emulsifier, an oil in water emulsion is formed. But if a soap with a bivalent cation is employed, say calcium oleate, a water in oil type emulsion is obtained. If to an oil in water emulsion stabilised by sodium oleate, a calcium or magnesium salt is added, the emulsion tends to be unstable at a particular concentration ratio of $\text{Na}^+ : \text{Ca}^{++}$. If the concentration of Ca^{++} be quickly increased, the inversion of the type of emulsion occurs and water-in-oil emulsion is produced.

In order to ascertain the type of a given emulsion, a small quantity of water is added with stirring and the effect is observed under a microscope. If the emulsion is oil-in-water type, water would mix freely with the excess medium, the droplets remaining undisturbed. If it is a water-in-oil type one, the addition of oil to the emulsion would produce similar effect. Sometimes addition of a small quantity of an electrolyte helps. If water be the dispersion medium, the conductance will increase but if oil be the medium, the effect on conductance on the addition of electrolyte would be negligible.

In many respects emulsions have characteristic properties similar to those of lyophobic colloids. The brownian motion and Tyndall phenomenon are observed with emulsion, as also the electrophoretic motion under an applied field. The

globules are negatively charged usually and these move towards the anode. The dispersed droplets are very sensitive to electrolytes and are easily 'salted out' with polyvalent cations.

Emulsions are most commonly broken up by brisk centrifuging, just as is universally done in separation of cream from milk. Freezing or boiling is also sometimes resorted to. One method of breaking up emulsions is to remove or change the emulsifier by adding external reagents. When soaps are used as emulsifying agents, if the same are hydrolysed by adding acids, the emulsion would easily break.

The formation of emulsions is now usually explained with the help of "adsorption film theory" proposed by Bancroft. It is believed that the emulsifying agent forms an adsorbed film on the surface separating the two liquids. This film is in contact with two phases, oil and water, and has two surface tensions. As a result the film will curve towards the phase on the surface of which tension is higher (Fig. XVI.14). The result is the dispersed liquid will be on the side of the film with higher surface tension. When univalent-cation-soap, like Na-oleate, is used, it is preferentially adsorbed or more wetted by water, than by oil. The surface tension is lower on the water side than on the oil-side. Spontaneously to reduce the area of the higher surface tension, the film curves the oil into droplets producing oil-in-water emulsion. On the other hand, when calcium or aluminium soaps are used, these are more easily wetted by the oil than by water. As a result, the water-surface is curved and water-in-oil type emulsions are formed.

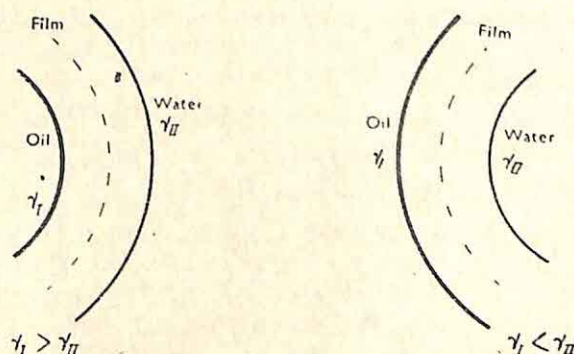


FIG. XVI.14 Formation of emulsions

Fine powders may also act as emulsifying agents, hydrated silica is used for obtaining water-in-oil type emulsion, where as carbon black is employed to prepare oil-in-water types. An intensive study of emulsions is now encouraged for their varied applications in food, drug and other industries. For example, in the concentration of ores by oil-floatation method, the finely pulverised ore is treated with an oil emulsion such that the required constituent is preferentially adsorbed on the interface for convenient collection.

References for further reading

1. 'Colloid Science'—Alexander and Johnson
2. 'Colloid Science'—Kruyt
3. 'Colloid Science'—Kraemer
4. 'Physical chemistry of colloidal solutions'—Burton
5. 'Physical chemistry of macromolecules'—Tanford
6. 'Principles of polymer chemistry'—Flory
7. 'Colloid Science'—McBain

Problems

1. The observed osmotic pressures of a polymer in benzene at 25°C were found to be :

conc (gms/100 c.c.)	0.50	1.00	1.25	1.50	2.00
π gms/cm ²	0.505	1.03	1.27	1.58	2.16

 find the number average mol. wt. (1 atmos = 1033 gm/cm²)

2. The sedimentation coefficient and diffusion coefficient of insulin are 3.5×10^{-13} sec and 8.2×10^{-7} cm²/sec respectively. The specific volume $v = 0.75$ c.c./gm and density, $\rho_{H_2O} = 0.998$ gms/c.c. Calculate the mol. wt. of insulin.

3. Calculate the sedimentation coefficient of an enzyme if in an ultracentrifuge a boundary moves 0.62 cms per hour when the speed is 12000 rpm from the centre of rotation 8 cms away.

4. What is the diffusion coefficient of the particles in an aqueous colloidal solution at 25°C if their mean radius be $20\text{\AA}$? The viscosity of the solution is assumed to be the same as that of water.

5. The mol. wt. of an albumin is 50000. Calculate the freezing point depression and osmotic pressure of its solution containing 10 gms/litre at 27°C.

6. A sample of polystyrene dissolved in toluene gave the following flow-times in an Ostwald viscometer at 25°C.

conc. gms/100 c.c.	0	0.1	0.3	0.6
time in sec.	86	99.5	133	195

Find out the intrinsic viscosity and hence mol. wt. assuming $k = 1.03 \times 10^{-4}$ and $a = 0.74$.

7. In a sedimentation egm with a gold sol, there were 889 particles/c.c. at a certain height of 40 mm from the bottom and 108 particles/c.c. at a height of 41 mm. Assuming spherical shape, show that mean value of their radii is $227\text{\AA}$. [density of gold, 19.3 gm/c.c.]

8. In the eqm. distribution of a gold sol particles in the gravitational field, the following data were recorded :

radius of particles = $625\text{\AA}$

$$\Delta h = h_2 - h_1 = 44.4\mu$$

density of gold = 19.32 gm/c.c., density of water = 0.899 gm/c.c.

no. of particles ; $n_1 = 328.9$ and $n_2 = 40.4$

Show that Avogadro number is 6.19×10^{23} .

PHOTOCHEMISTRY

XVII.1. Photochemical Reactions. The reactions ordinarily carried out in the laboratory and whose mechanisms and kinetics have been considered in Chapter XV are 'thermal' or 'dark' reactions. In these reactions, the activation energy is obtained through collisions. The average kinetic energy of translation ($3/2 RT$) is of the order of 1000 calories and is not sufficient for chemical transformation. The energies needed for chemical reaction are in the range 10^4 – 10^5 calories per mole approximately. But we know from the distribution law, some molecules at any instant would possess sufficiently large an amount of energy and these are the ones which suffer chemical change in an ordinary thermal process.

The activation may also be effected by providing the necessary energy from other sources, such as from collision with photons of visible, ultraviolet rays or of X-rays or γ -rays. A *photon* of radiation, also often called quantum, is a primary unit of radiation and is given by $h\nu$. Besides photons, high energy particles like α -ray, β -ray or protons, neutrons etc. from cyclotrons or reactors may be used for activation purposes.

When the chemical changes occur directly or indirectly in consequence mainly of absorption of photons from visible and ultraviolet radiations having wavelengths from about 10000 Å to 1000 Å, the reactions are called *photochemical* reactions. The energy in this range varies from 1 ev to 10 ev or 23 to 230 kilocalories per mole. *Photochemistry* therefore concerns itself with reaction effected with the help of visible or ultraviolet radiations.

On the other hand if a photon from X-ray tube or a γ -ray photon be used, or if high energy particles α -rays, protons, neutrons be employed, innumerable molecules coming in their path would be ionised, their energy content being very high. These ionisations would lead to chemical changes through secondary processes. For example, when a γ -ray photon of an approximate energy value of 1 mev passes through a medium, extensive ionisation of the molecules takes place. With a photon from visible or ultraviolet source, the ionisation occurs but seldom. α , β , γ -rays, protons, neutron beams etc. are therefore called ionising radiations. The study of the effect of these radiations therefore comes in the field of what is now called *Radiation chemistry*.

The energy involved in visible radiations is in the range 35000 to 72000 calories and that in the ultraviolet region in the range 72000 to 286000 calories per mole. [See the energy values of different radiations given in the table below and also see Fig. VII.10.] The absorption of these visible and ultraviolet radiations may, under suitable conditions, lead to direct chemical changes.

TABLE : ENERGY OF DIFFERENT RADIATIONS

Wave length λ (Å)	Frequency ν	Description	Energy per mole in	
			calories	ev
10^5	3×10^{13}	Infra red	2860	
10^4	3×10^{14}	Near infra red	28600	0.12
8000	3.75×10^{14}	Red	35700	1.24
5000	6×10^{14}	Blue	56900	1.55
4000	7.5×10^{14}	Violet	71500	2.48
1000	3×10^{15}	Ultra violet	286000	3.10
1	3×10^{18}	X-rays	2.86×10^8	12.4
0.01	3×10^{20}	γ -rays	2.86×10^{10}	12400
				1.24×10^6

There are some noteworthy differences between the thermal and the photochemical reactions. In thermal reactions, the temperature coefficient is generally

large. In a photochemical process, the intensity of light introduced from an external source does not depend on the temperature of the reacting system. As such the primary process of photoactivation has a very low temperature coefficient.

Moreover, the occurrence of thermal reactions is always accompanied by a free energy decrease. But there are a number of well known photochemical reactions in which an increase of the free energy is involved. Remembering that photochemical processes may be non-spontaneous, such increase in free energy is not ruled out; the photon absorbed may increase the free energy of the reactants sufficiently to make ΔG negative. The *photosynthesis* of carbohydrate through chlorophyll and sunlight is an outstanding example where the transformation involves free energy increase. Other instances are polymerisation of anthracene, decomposition of ammonia, etc.

XVII.2. Laws of Photochemistry. The photochemical reactions are governed by two basic principles, the Grotthus-Draper law and the Einstein law of photochemical equivalence.

A. The *Grotthus-Draper law states that only those radiations which are absorbed can be effective in producing the chemical change*. It does not necessarily mean that all, or any, of the light would be effective in causing chemical change. In many cases, the energy absorbed is rendered into heat; in other cases the absorbed energy is re-emitted as radiations of some other frequencies. An interaction between an approaching photon of radiation and a molecule would occur only when there is some simple electronic, atomic or molecular motion which can use up the exact amount of energy contained in the photon of radiation. If there be no such change or motion within the molecule, there shall be no absorption and, hence, no physical or chemical change. The photon will be absorbed if there be within the molecule some change which is not forbidden by quantum restrictions and which corresponds to the energy contained in the photon. After the energy is received by a molecule the same may be given up to other molecules by collisions increasing the kinetic energy. The net result is rise of temperature from the conversion of the radiation absorbed into thermal energy.

The extent of absorption of radiation is related to the depth (l) of the absorbing material, the relation being expressed by Lambert's law,

$$I = I_0 e^{-kl} \quad \dots \text{(VII.42)}$$

where k is the 'absorption coefficient' and I -terms are intensities. In the case of a solution, the quantitative relation between the amount of absorption of light and concentration (c) is given by Beer's law, as

$$I = I_0 10^{-\epsilon cl} \quad \dots \text{(VII.45)}$$

where ϵ is the "molar extinction coefficient." These relations have been discussed already in Sec. VII.20.

B. In 1912, Einstein extended the concept of quantum theory of radiation to photochemical processes. The principle states that "*each quantum of radiation absorbed by a molecule activates one molecule in the primary step of a photochemical process.*" This is known as the Einstein's law of photochemical equivalence.

The law is concerned with the primary step of activation of the molecule. If every molecule so activated in the primary absorption directly decomposes, the number of reactant molecules suffering chemical change would be equal to the number of quanta of energy absorbed. But the primary photon absorption activated photochemically may initiate a sequence of reactions so that many reactant molecules through a chain mechanism would undergo chemical change. In such cases, the number of reactant molecules transformed will be many times the quanta of energy absorbed. In some cases, where quick deactivation takes place, the number of reactant molecules suffering change would be less than one per quantum. Einstein's law therefore should not be interpreted to mean that one molecule would react per quantum of light absorbed, but that only one molecule is activated by each quantum of radiation.

The efficiency of a photochemical process is often expressed in terms of *quantum yield* (ϕ), which is defined as the number of molecules reacting per quantum of light absorbed, i.e.,

$$\phi = \frac{\text{no. of molecules reacting}}{\text{no. of quanta of radiation absorbed}}$$

If the light absorbed has a frequency ν per sec or wavelength λ in cms, then its energy is $h\nu$ ergs. The energy absorbed per mole, according to the law of photochemical equivalence, is

$$E = N_0 h \nu = \frac{N_0 h c}{\lambda} \text{ ergs per mole} \quad \dots (\text{XVII.1})$$

Since $c = 2.998 \times 10^{10}$ cms/sec, $h = 6.625 \times 10^{-27}$ ergs-sec and $N_0 = 6.02 \times 10^{23}$,

$$\text{we have, } E = \frac{1.196 \times 10^8}{\lambda} \text{ ergs per mole} \quad \dots (\text{XVII.2})$$

If λ be expressed in Angstrom units, ($1 \text{ \AA} = 10^{-8}$ cms),

$$E = \frac{1.196 \times 10^{16}}{\lambda} \text{ ergs per mole} \quad \dots (\text{XVII.3})$$

$$\begin{aligned} \text{or, } E &= \frac{1.196 \times 10^{16}}{\lambda \times 4.184 \times 10^7} \text{ calories per mole} \\ &= \frac{2.859 \times 10^5}{\lambda} \text{ kilocalories per mole} \quad \dots (\text{XVII.4}) \end{aligned}$$

This energy (E) which activates one mole of the reactant i.e., the energy corresponding to Avogadro number of photons is called '*one einstein*'. It is evident the energy will be greater lower the wavelength. So an einstein corresponding to violet or ultraviolet radiations would involve more energy than one in the visible red region.

Example. Calculate the energy in ergs, calories and electron volts in ultraviolet light of wavelength 2000 Å absorbed per mole.

$$\begin{aligned} (a) \quad E &= \frac{1.196 \times 10^{16}}{\lambda} = \frac{1.196 \times 10^{16}}{2000} \text{ ergs per mole (from eqn. XVII.3)} \\ &= 5.98 \times 10^{12} \text{ ergs/mole.} \end{aligned}$$

$$(b) \quad E = \frac{5.98 \times 10^{12}}{4.184 \times 10^7} \text{ calories per mole} = 1.43 \times 10^5 \text{ cal/mole}$$

$$(c) \quad \text{Since } 1 \text{ e.v.} \equiv 23060 \text{ cal, } E = \frac{1.43 \times 10^5}{23060} = 6.2 \text{ e.v./mole}$$

The quantum yield of some well-studied photochemical reactions are given below.

QUANTUM YIELD OF PHOTOCHEMICAL REACTIONS

Reactions	Wavelength (Å)	ϕ (quantum yield)
$2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$	2100	
$\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$	4200	0.25
$2\text{HBr} = \text{H}_2 + \text{Br}_2$	2070–2530	1.0
$2\text{HI} = \text{H}_2 + \text{I}_2$	2070–2820	2.0
$(\text{CH}_3)_2\text{N}_2 = \text{C}_2\text{H}_6 + \text{N}_2$	3660	2.0
$2\text{NO}_2 = 2\text{NO} + \text{O}_2$	3660	2.0
$\text{CO} + \text{Cl}_2 = \text{COCl}_2$	4000–4360	1.5
$\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$	4000–4360	$< 10^3$
maleic acid $\rightarrow$ fumaric acid	2000–2800	$< 10^6$
$\text{CH}_2\text{ClCOOH} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{OHCOOH} + \text{HCl}$	2537	0.04
		1.0

Experimental arrangement. A schematic representation of the experimental arrangement required in studying photochemical reactions is given in Fig. XVII.1. The reactants are taken in a glass or quartz cell X whose walls are optically plane. The cell is kept in a constant temperature bath D . From the light source (L) the radiations are passed through a condenser system (A) when a parallel beam is formed. Different gas-discharge tubes, metal-arcs, filament-lamps are used as light source (L) depending upon the required spectral range. The parallel beam then passes through a filter or monochromator B , so that a beam of only definite wavelength may come out to enter the reaction vessel (X) after its passage through the slit C and window (W_1).

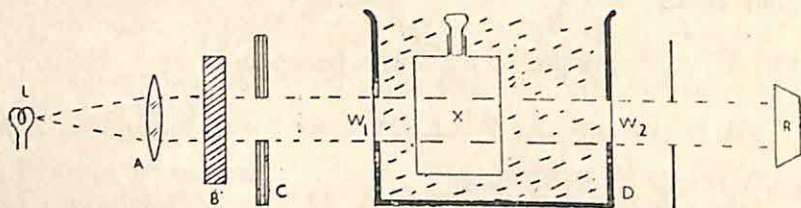
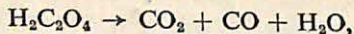


FIG.XVII.1 Experimental arrangement for studying photochemical reactions (schematic)

After absorption in the reaction vessel, the residual portion of the radiations passes through the window (W_2) and finally enters a photocell or thermopile etc. in which the intensity of the radiation could be measured. When ultraviolet radiations are used, all transparent parts are made of quartz.

The intensity of the radiations is estimated with the help of *photocells, or better, thermopiles*. The thermopiles are multi-thermocouple junctions and these are previously calibrated against standard light sources. So when any radiation falls on them, the intensity of the same is known. Sometimes *chemical actinometers* are employed. These contain reactants sensitive to light. A commonly used actinometer is the uranyl oxalate actinometer in which a mixture of 0.04 M oxalic acid and 0.01 M uranyl sulphate is taken. On exposure to radiation, the change,



occurs. The amount of reaction is measured by titrating back the residual oxalic acid with permanganate. The uranyl ion does not change. In the wavelength range of 2540 – 4350 Å each mole of oxalic acid decomposed is equivalent to 1.75 einsteins ($= 1.66 \times 10^5$ calories). The intensity in the experiment concerned is evaluated from this standard value.

The reaction rate is measured by the usual methods of study as in chemical kinetics. Small quantities of samples are pipetted out from time to time and analysed. Or, the change in some physical property, such as optical rotation or absorption or refractive index, is followed to determine the rate equation and the quantum yield (ϕ).

Example. On irradiation of propionaldehyde at 30°C with light of $\lambda = 3020 \text{ Å}$, the quantum yield for CO is found to be 0.54. The intensity of incident light is 15000 ergs/sec. What is the light intensity in einsteins per sec? Also find out the rate of formation of CO.

$$\text{At } \lambda = 3020 \text{ Å, one einstein} = \frac{1.196 \times 10^{16}}{3020} \text{ ergs/mole}$$

$$\therefore 15000 \text{ ergs} \equiv \frac{15000 \times 3020}{1.196 \times 10^{16}} = 3.78 \times 10^{-9} \text{ einstein}$$

$$\text{Now, quantum yield } \phi = \frac{\text{no. of molecules reacting}}{\text{no. of quanta absorbed}} = \frac{\text{no. of moles reacting}}{\text{no. of einsteins absorbed}}$$

$$\text{or } \phi = 0.54 = \frac{\text{no. of moles reacting}}{3.78 \times 10^{-9}}$$

$$\text{Hence, rate of formation of CO} = 0.54 \times 3.78 \times 10^{-9} = 2.04 \times 10^{-9} \text{ moles/sec.}$$

XVII.3. Primary Processes in Photochemical Reactions. The first step in a photochemical process is the absorption of energy of the radiation by the molecule. The energy obtained from a photon in the visible or ultraviolet region leads to an electronic transition (Chapter VII). The primary process therefore consists in raising the electronic quantum level of the molecule by absorption of energy. The energy-rich or the excited molecule may then behave in different ways. If

the excited molecule re-emits the absorbed energy, wholly or partly, in order to come back to the ground state, *fluorescence* or *phosphorescence* may occur to which we shall refer later. In many an instance, the excess energy gained by the molecule may be transferred to other molecules by collision, resulting into kinetic energy. In effect, the energy of the photon is transformed into *heat*, the temperature of the absorbing system is raised. But the excited molecule may behave in other ways leading to chemical changes. Such behaviour may be more easily followed from potential energy curves.

The electronic transition, which occurs on absorption of energy, is accompanied with changes in vibrational and rotational quantum levels and is governed by Franck-Condon principle (Sec. VII.16). Broadly speaking, there are four distinct possibilities from the excitation of the molecules, as depicted in Fig. XVII.2.

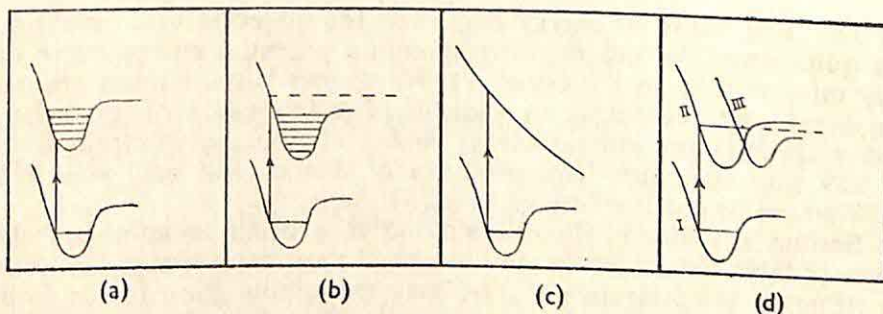
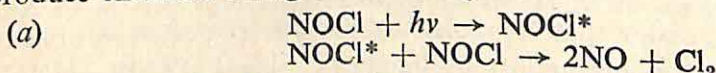
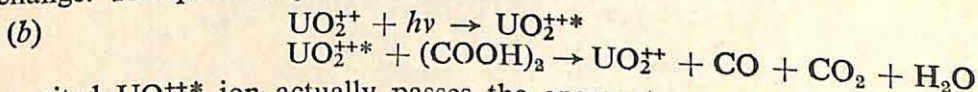


FIG. VII.2 Photochemical Primary Process (Pot. energy curves)

(i) When the molecule in the higher electronic level also assumes a definite vibrational level as shown in curve (a), there shall be no direct dissociation of the molecule. This will be revealed from the fine structure of the electronic band spectra of the molecule. The excess energy, in the usual course, may be dissipated as heat or may give rise to fluorescence etc. But the molecule may retain its energy until it can be used chemically (a) by combination with another molecule or (b) by transferring the energy to another molecule which in turn utilises the energy to produce chemical change. For example :



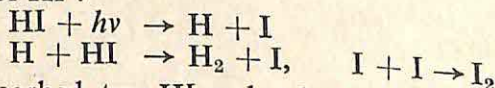
Here, the excited NOCl^* reacts with a normal molecule of NOCl leading to a chemical change. The quantum yield is 2.



The excited UO_2^{++*} ion actually passes the energy to an oxalic acid molecule, which suffers decomposition. *asterisk indicates an activated molecule.

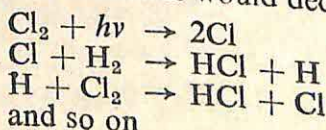
(ii) If the molecule raised to the higher electronic state acquires a quantum level above the maximum stability level, the energy acquired is higher than the binding energy concerned ; the molecule in its first oscillation will undergo dissociation (curve b). The spectrum will show a continuum. The products of dissociation may enter into a simple thermal chemical process or these may start chain reactions. Sometimes the energy taken up by a particular portion or bond in the molecule may be transferred to another bond in the same molecule leading to the dissociation. A few typical illustrations are given.

(a) Decomposition of HI :



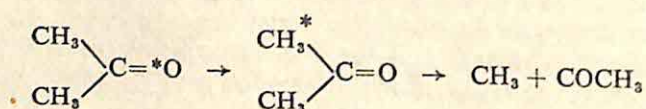
Thus, for each photon absorbed, two HI molecules would decompose.

(b) $\text{H}_2 - \text{Cl}_2$ reaction :

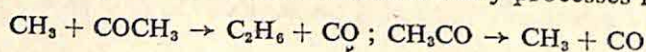


A chain process would continue from the primary process of dissociation. The chain may terminate as $\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$. The quantum yield is high.

(c) Photolysis of acetone :



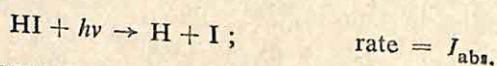
The photon absorption primarily occurs at the $\text{C}=\text{O}$ and subsequently, on transfer, leads to the cleavage of $\text{C}-\text{C}$ bond. The existence of the free radicals has been experimentally demonstrated. The secondary processes follow mainly as,



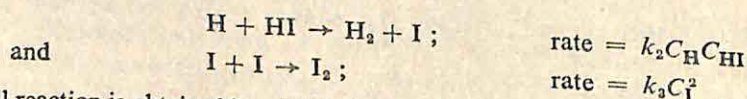
(iii) The absorption of energy may raise the molecule to an electronic state which is quite unstable and the corresponding potential energy curve does not show any minimum as in the curve (c). No sooner is the photon absorbed, the molecule breaks up into atom or radicals. The fragments of dissociation are produced with different kinetic energy and a continuous spectrum is obtained without any fine structure. The products of dissociation may start secondary chemical changes or chain reactions as in (ii) above.

(iv) Besides the above, the dissociation may occur in another fashion. By absorption of light the molecule may be raised to a stable higher electronic state. But sometimes a third electronic state may exist quite close to the former and intersecting with it (curve *d*). In consequence, when the oscillations are relatively slow, there is a chance of the molecule of shifting from the stable (II) to the unstable state (III). When such shift takes place, the molecule would dissociate producing atoms or radicals. The spectrum would show fine structure at lower levels of vibrations followed by a continuum; the latter may be followed by fine structure again. This is predissociation as discussed in Sec. VII.16. We may now consider some typical cases.

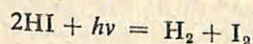
XVII.4. Some Typical Photochemical Reactions. (i) *Decomposition of hydrogen iodide.* The electronic spectrum of HI in the wave length range $2000 \text{ \AA}$ to $3300 \text{ \AA}$ shows a continuum, indicating that HI molecules are dissociated in this region by absorption of radiation. The decomposition has been studied at 2820 and $2530 \text{ \AA}$. The primary step is thus regarded as



This is followed by secondary processes,



The overall reaction is obtained by adding the three steps ;



The rate of the net reaction should be

$$\frac{-dC_{\text{HI}}}{dt} = I_{\text{abs}} + k_2 C_{\text{H}} \cdot C_{\text{HI}} \quad \dots (a)$$

Under steady-state condition, $\frac{dC_{\text{H}}}{dt} = 0$,

$$\text{i.e.,} \quad \frac{dC_{\text{H}}}{dt} = I_{\text{abs}} - k_2 C_{\text{H}} \cdot C_{\text{HI}} = 0 \quad \dots (b)$$

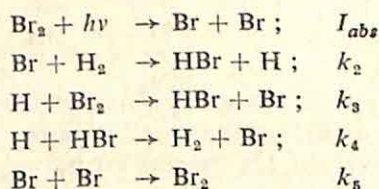
Adding (a) and (b),

$$\frac{-dC_{\text{HI}}}{dt} = 2 I_{\text{abs}}$$

This means that two moles of HI would decompose per einstein of radiation absorbed. This is confirmed from experimental results. The mechanism proposed therefore is justified.

(ii) *Hydrogen-bromine reaction.* With radiations of wavelengths less than 5100 Å, the banded spectrum of bromine disappears and a continuum is obtained. Bromine molecules are therefore dissociated into atoms by absorption of such radiations. The mechanism of the photochemical reaction between hydrogen and bromine is represented as,

rate constants



This is the same as proposed for the thermal process in Sec. XV.18. The rate of formation of HBr is given by

$$\frac{dC_{\text{HBr}}}{dt} = k_2 C_{\text{H}_2} \cdot C_{\text{Br}} + k_3 C_{\text{H}} \cdot C_{\text{Br}_2} - k_4 C_{\text{HBr}} \cdot C_{\text{H}} \quad \dots (A)$$

Under steady-state conditions, $\frac{dC_{\text{H}}}{dt} = 0$, $\frac{dC_{\text{Br}}}{dt} = 0$. We have,

$$\frac{dC_{\text{H}}}{dt} = 0 = k_2 C_{\text{H}_2} \cdot C_{\text{Br}} - k_3 C_{\text{H}} \cdot C_{\text{Br}_2} - k_4 C_{\text{HBr}} \cdot C_{\text{H}} \quad \dots (B)$$

and
$$\frac{dC_{\text{Br}}}{dt} = 0 = 2I_{\text{abs}} - k_2 C_{\text{H}_2} \cdot C_{\text{Br}} + k_3 C_{\text{H}} \cdot C_{\text{Br}_2} + k_4 C_{\text{H}} \cdot C_{\text{HBr}} - k_5 C_{\text{Br}}^2 \quad \dots (C)$$

Adding (B) and (C), $2I_{\text{abs}} = k_5 C_{\text{Br}}^2$

or
$$C_{\text{Br}} = \sqrt{\frac{2I_{\text{abs}}}{k_5}} \quad \dots (D)$$

Substitution of this in (B), and simplifying,

$$C_{\text{H}} = \frac{k_2 \left(\frac{2I_{\text{abs}}}{k_5} \right)^{\frac{1}{2}} C_{\text{H}_2}}{k_3 C_{\text{Br}_2} + k_4 C_{\text{HBr}}} \quad \dots (E)$$

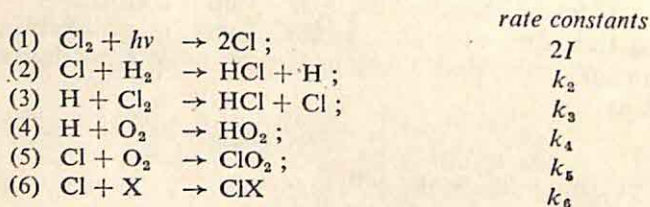
Again substituting (D) and (E) in (A)

$$\frac{dC_{\text{HBr}}}{dt} = \frac{2k_2 \left(\frac{2I_{\text{abs}}}{k_5} \right)^{\frac{1}{2}} C_{\text{H}_2}}{1 + [k_4 C_{\text{HBr}} / k_3 C_{\text{Br}_2}]} \quad \dots (F)$$

It is the same rate as given in the thermal reaction by equation (XV.51), in which the factor $(2 I_{\text{abs}}/k_5)$ replaces $k_6 C_{\text{Br}_2}^{\frac{1}{2}}$. It is thus seen that both in thermal and in photochemical reactions, the primary process is the dissociation of bromine molecule. The dissociation occurs through kinetic energy in thermal reaction and through absorbed radiation in photochemical reaction. That is why higher temperature is needed for the thermal process.

(iii) *Hydrogen-chlorine reaction.* A chain mechanism, as in hydrogen-bromine reaction, has also been observed in the photochemical reaction. But the hydrogen-chlorine reaction rate is profoundly influenced by traces of various impurities, especially oxygen. The reaction starts with the primary dissociation of Cl_2 molecules on absorption of radiations of wavelengths below 4800 Å. Different schemes

to explain the reaction-rate had been proposed by different investigators. Of these the most satisfactory mechanism had been proposed by Göhring (1921), which is expressed as follows :



'X' is a foreign body, may be the wall, which removes chlorine atoms. In fact, the last three steps serve as chain-breakers or inhibitors.

On the steady-state principle, the rate of formation of chlorine and hydrogen atoms may be written as,

$$\frac{dC_{\text{Cl}}}{dt} = 2I - k_2 C_{\text{H}_2} \cdot C_{\text{Cl}} + k_3 C_{\text{Cl}_2} \cdot C_{\text{H}} - k_5 C_{\text{Cl}} C_{\text{O}_2} - k_6 C_{\text{Cl}} C_{\text{X}} = 0 \quad \dots (A)$$

$$\frac{dC_{\text{H}}}{dt} = k_2 C_{\text{H}_2} \cdot C_{\text{Cl}} - k_3 C_{\text{Cl}_2} \cdot C_{\text{H}} - k_4 C_{\text{O}_2} \cdot C_{\text{H}} = 0 \quad \dots (B)$$

$$\therefore \text{ From (A), } C_{\text{Cl}} = \frac{2I + k_3 C_{\text{H}} \cdot C_{\text{Cl}_2}}{k_2 C_{\text{H}_2} + k_5 C_{\text{O}_2} + k_6 C_{\text{X}}} \quad \dots (C)$$

$$\text{and from (B), } C_{\text{Cl}} = \frac{k_3 C_{\text{H}} \cdot C_{\text{Cl}_2} + k_4 C_{\text{O}_2} \cdot C_{\text{H}}}{k_2 C_{\text{H}_2}} \quad \dots (D)$$

Equating (C) and (D),

$$k_2 C_{\text{H}_2} (2I + k_3 C_{\text{Cl}_2} \cdot C_{\text{H}}) = (k_2 C_{\text{H}_2} + k_5 C_{\text{O}_2} + k_6 C_{\text{X}}) (k_3 C_{\text{H}} \cdot C_{\text{Cl}_2} + k_4 C_{\text{O}_2} \cdot C_{\text{H}})$$

Neglecting $k_4 k_5 C_{\text{O}_2}^2 \cdot C_{\text{H}}$ which is indeed very small we have,

$$C_{\text{H}} = \frac{2Ik_2 C_{\text{H}_2}}{k_3 k_6 C_{\text{Cl}_2} \cdot C_{\text{X}} + C_{\text{O}_2} \{k_2 k_4 C_{\text{H}_2} + k_3 k_5 C_{\text{Cl}_2} + k_4 k_6 C_{\text{X}}\}} \quad \dots (E)$$

This relation is much simplified when the impurity oxygen is extremely small, say less than 0.004 cms pressure. In such conditions, we have

$$C_{\text{H}} = \frac{2I k_2 C_{\text{H}_2}}{k_3 k_6 C_{\text{X}} \cdot C_{\text{Cl}_2}} \quad \dots (F)$$

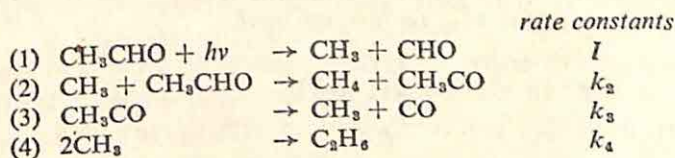
The rate of over-all formation of HCl is mainly dependent on the step (3), $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$. The step (2) is extremely slow. This is revealed from consideration of activation energies. Hence, the rate of formation of HCl may be taken as,

$$\begin{aligned} \frac{dC_{\text{HCl}}}{dt} &= k_3 C_{\text{H}} \cdot C_{\text{Cl}_2} \\ &= k_3 \cdot \frac{2I k_2 C_{\text{H}_2}}{k_3 k_6 C_{\text{X}}} = k \cdot I \cdot C_{\text{H}_2} \quad \dots (G) \end{aligned}$$

for C_{X} is supposed to remain constant. The relation (G) has been corroborated from experimental results, with negligible conc. of oxygen. The rate is thus independent of chlorine concentration.

When small amounts of oxygen are present Bodenstein and Unger (1930) have shown that generally eqn. (G) is followed by the reaction.

(iv) *Decomposition of acetaldehyde.* The decomposition of acetaldehyde on absorption of ultraviolet radiations ($\lambda < 3000 \text{ \AA}$) is an example of a photochemical process where the molecule is first excited to a higher quantum level and then it breaks up into radicals which start chain reactions. The mechanism is given as,



The rate of formation of CO is, $\frac{dC_{\text{CO}}}{dt} = k_3 C_{\text{CH}_3\text{CO}} \dots (A)$

Applying the steady-state principle to rates of formation of CH_3CO and CH_3 radicals, we have

$$\frac{d}{dt} C_{\text{CH}_3\text{CO}} = k_2 C_{\text{CH}_3} \cdot C_{\text{CH}_3\text{CHO}} - k_3 C_{\text{CH}_3\text{CO}} = 0$$

$$\text{or} \quad C_{\text{CH}_3\text{CO}} = \frac{k_2}{k_3} C_{\text{CH}_3} \cdot C_{\text{CH}_3\text{CHO}} \dots (B)$$

$$\text{And} \quad \frac{d}{dt} C_{\text{CH}_3} = I - k_2 C_{\text{CH}_3} \cdot C_{\text{CH}_3\text{CHO}} + k_3 C_{\text{CH}_3\text{CO}} - k_4 C_{\text{CH}_3}^2 = 0$$

$$\text{or} \quad C_{\text{CH}_3} = \left(\frac{I}{k_4} \right)^{\frac{1}{2}} \dots (C)$$

Inserting (B) and (C) in (A), the rate of formation of CO is

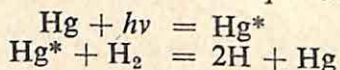
$$\frac{d}{dt} C_{\text{CH}_4} = k_2 \left(\frac{I}{k_4} \right)^{\frac{1}{2}} C_{\text{CH}_3\text{CHO}} = k \cdot I^{\frac{1}{2}} \cdot C_{\text{CH}_3\text{CHO}}$$

This relation has appreciable support from experimental result. [See Blacet and Loeffler, J. Am. Chem. Soc. 64, 893, 1942.]

XVII.5. Photosensitized Reaction. Photosensitized reactions constitute a separate group of photochemical reactions. In these reactions, the reactants are insensitive to the light to which they are exposed and as such these reactants do not take part in the primary step of absorption of radiation and dissociation. However when a suitable foreign matter is mixed with the reactants, the former will absorb the radiation and become excited. Subsequently, the excited foreign matter will pass on the energy to the reactant molecules which will undergo dissociation or chemical transformation. Processes of this nature are termed *photosensitized reactions* and the foreign substance which absorbs and transfers the energy of radiation is called the *photosensitizer*. Mercury or cadmium vapours are often used as sensitizers.

To illustrate, when a mixture of H_2 and O_2 is exposed to radiations from a mercury lamp, $\lambda = 2537 \text{ \AA}$, there is no change observed. The energy of the radiation corresponding to this wavelength is 112000 calories. The energy required to dissociate a hydrogen molecule is 103200 calories and an oxygen molecule is 117200 calories. The energy from the given radiation is insufficient to dissociate O_2 -molecule. But for hydrogen, this energy is sufficient, yet the H_2 -molecule will not dissociate as it is insensitive to this radiation. For dissociation by absorption of radiation, the wavelength must be in its absorption continuum. In the case of hydrogen, the continuous spectrum begins below $\lambda = 849 \text{ \AA}$. The presence of sufficient energy is not the only criterion for dissociation. The absorption is

governed by the selection rules. That is why H_2 -molecule will not dissociate with radiation $\lambda = 2537 \text{ \AA}$. Now if a small amount of mercury vapour is mixed with the reactants, the mercury atoms take up the radiation and become excited atoms. The excited mercury then transfers this energy (112000 cal) by collision to hydrogen dissociating it. In this dissociation about 103000 cal are used up, the residual amount of energy is utilised in increasing translational energy. By transferring this energy, the excited mercury atom is said to be *quenched*.

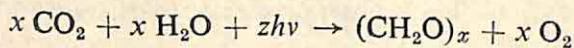


The atomic hydrogen so produced will then carry on with the usual chain reactions to produce water.

Amongst many other mercury-photosensitized reactions, we may mention decomposition of ammonia, arsine, various alcohols, acids, etc.; hydrogenation of ethylene, carbon monoxide, etc.

That photochemical decomposition of oxalic acid is sensitized by UO_2^{++} ion has been mentioned earlier (Sec. XVII.3). Chlorine is a good sensitizer for the synthesis of water, ozone, or in the reaction, $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$, the radiations used has $\lambda = 4300 \text{ \AA}$.

The most outstanding example of photosensitization is the photosynthesis of carbohydrates in plants, in which the green colouring matter chlorophyll is the photosensitizer. Chlorophyll absorbs visible light in the region $6000-7000 \text{ \AA}$ and this absorbed energy is then passed on to the reactants ($\text{CO}_2 + \text{H}_2\text{O}$) to form the basic molecule of the carbohydrate as

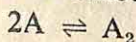


The exact process is a very complicated one and the true mechanism of the reaction is not clear. It is however found that the energy corresponding to radiations absorbed is about 40 kcal where as the energy needed in the transformation of one mole of CO_2 is about 112 kcal. This means that several quanta are required for the transformation of each molecule of CO_2 and H_2O taking part.

Ghosh and his co-workers studied the photochemical oxidation-reduction of different systems using inorganic sols as photosensitizer. For example, using ultraviolet rays (366 and $333 \mu\mu$), glucose was oxidised by iodine in presence of tungstic acid sol. It was established that the sol first absorbs the light which is then transferred to iodine causing the dissociation of the latter. The iodine atom subsequently oxidises the sugar. The quantum efficiency was $1.8-0.74$.*

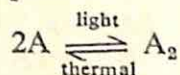
A very interesting use of photosensitization is found in photography now-a-days. The silver halide emulsion used in photo-films are insensitive to longwave radiations. Some dyes are now added to the emulsion, which absorb longer wave radiations and transfer the energy to the silver halides. The result is even in the absence of visible light the emulsion would undergo the change. The infra-red photography is thus rendered possible through the dye sensitizers.

XVII.6. Photochemical Equilibrium. The chemical equilibrium of a thermal reversible process is greatly influenced if light is absorbed either in the forward or backward process. Thus the absorption of light by the reactant in the forward process will increase the speed of the forward reaction, but will not influence the rate of reverse thermal reaction. Due to increased concentration of the products, the rate of the reverse thermal process may increase to some extent. Ultimately however a balance between the rates of forward and backward reactions will be reached, equilibrium. This balanced state is not really the true equilibrium state of the system but is existent in presence of light. This is a stationary state, often called a *photostationary equilibrium*. The best example to illustrate this phenomenon is the dimerization of anthracene. If 'A' denotes an anthracene molecule, the reaction is



*Ghosh et al. J. Ind. Chem. Soc. 581, 14, 1937.

But the dimerization of anthracene in benzene solution can be carried out photochemically with ultraviolet light. The opposite change, the conversion of dimers into monomers is a thermal process.



The anthracene in solution on being irradiated with ultraviolet light absorbs a quantum and becomes excited. The excited molecule (A^*) forms a dimer by collision with a normal molecule. But the excited molecules may also re-emit the absorbed energy through fluorescence and be quenched. The different steps in the system are

			rates
(1)	$A + h\nu \rightarrow A^*$	(excitation)	I_{abs}
(2)	$A^* + A \rightarrow A_2$	(dimerisation)	$k_2 C_{A^*} C_A$
(3)	$A^* \rightarrow A + h\nu'$	(fluorescence)	$k_3 C_{A^*}$
(4)	$A_2 \rightarrow 2A$	(thermal)	$k_4 C_{A_2}$

Applying the steady-state principle, the concentration of A^* should be constant,

$$\text{i.e.,} \quad \frac{dC_{A^*}}{dt} = 0 = I_{abs} - k_2 C_{A^*} C_A - k_3 C_{A^*}$$

$$\text{or} \quad C_{A^*} = \frac{I_{abs}}{k_2 C_A + k_3}$$

$$\text{The rate of formation of the dimer } \frac{dC_{A_2}}{dt} = k_2 C_{A^*} C_A - k_4 C_{A_2}$$

$$\text{At the photostationary state, the conc. } C_{A_2} \text{ is constant, hence } \frac{dC_{A_2}}{dt} = 0$$

$$\begin{aligned} \therefore C_{A_2} &= \frac{k_2 C_{A^*} C_A}{k_4} = \frac{k_2 C_A I_{abs}}{k_2 k_4 C_A + k_3 k_4} \\ &= \frac{I_{abs}}{k_4 \left[1 + \frac{k_3}{k_2 C_A} \right]} \end{aligned}$$

When the concentration of anthracene is appreciable, there are greater chances of collision; the re-emission of energy through fluorescence as in step (3) is very small. So, with high concentration of anthracene (C_A being large), we have

$$C_{A_2} = I_{abs}/k_4$$

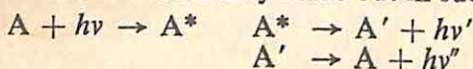
In other words, with a given radiation intensity, the concentration of the dimer at the photostationary state is constant. It is independent of the concentration of the monomer. But in a thermal equilibrium, $C_{A_2} = K C_A$ where K is the equilibrium constant. The difference between the normal equilibrium state and the photostationary equilibrium is easily seen. If the source of light be removed, the system will begin to change until the normal thermal equilibrium is attained.

Other instances of photostationary equilibria have also been studied such as the decomposition of NO_2 or of ozone.

XVII.7. Fluorescence and Phosphorescence. It is commonly noticed that if a metal is heated to high temperature, it first becomes 'red hot' and then 'white hot'. That is, the body is made to emit visible radiations through the application of heat. However, if such emission of radiations occurs from a body due to the application of agency other than heat, the emitted radiation is called *Luminescence*. Luminescence may be of different types such as fluorescence, phosphorescence, etc.

1. *Resonance radiation.* When an atom or molecule absorbs light, it is excited to a higher electronic level. If the absorbed energy is almost immediately emitted back within a time interval of about 10^{-8} seconds and the emitted radiation has the same frequency, it is called 'resonance radiation'. Such cases often are found with atoms absorbing light waves. $A + h\nu \rightarrow A^*$; $A^* \rightarrow A + h\nu$

2. *Fluorescence*. But if the emitted radiation has a frequency less than that of the absorbed radiation it is called 'fluorescence'. The absorbed energy shall be released within 10^{-8} seconds but it may come out in successive stages.



i.e., radiations of different frequencies may be emitted. The emission in fluorescence shall cease as soon as the light source is removed. Various fluorescent substances are well-known. The minerals fluorite, petroleum; the organic dyes like eosin, fluorescein; compounds like chlorophyll, ultramarine, riboflavin, etc. exhibit fluorescence either with visible light or ultraviolet irradiation.

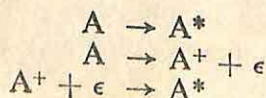
3. *Phosphorescence*. Certain molecules after being excited by absorption of visible or ultraviolet radiation emit the radiations slowly and even long after the light source is removed. This is known as 'phosphorescence'. Zinc sulphide, alkaline earth sulphides are good examples of such phosphorescent substances.

4. *Chemiluminescence*. If at ordinary temperatures, light is emitted as a result of chemical reactions, the phenomenon is termed chemiluminescence. At ordinary temperatures, emission of light is not expected from substances. The emission occurs at the expense of some amount of heat of reaction. A portion of the heat of reaction activates some molecules of the system and the excited molecules then emit the energy as radiation. The glow of yellow phosphorus in air at room temperature producing 'cold light' is a common laboratory experience. During the auto-oxidation of some Grignard reagents, or alkaline solution of 5-aminophthalic hydrazide etc. such chemiluminescence is observed. The glow of fireflies is due to the chemiluminescence of a protein (luciferin) oxidation by oxygen in presence of an enzyme. The decay of wood and vegetation over marshy places is often accompanied with chemiluminescence.

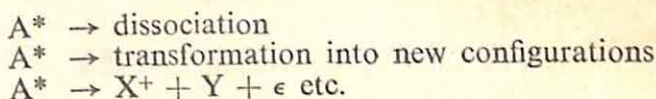
XVII.8. Radiation Chemistry. The use of radiations of high frequencies such as X-rays, γ -rays etc. or high-energy particles like protons, electrons, alpha particles, neutrons, etc. leads to very complicated results. In photochemical processes, the photons used have energies up to 150000 cal per einstein i.e., about 6.5 ev. But in high energy waves or particle beams, the energy will be of the order of 1 million electron volt or so. So in the primary process when a reactant is exposed to such rays, almost always ionisation occurs producing electrons and positive ions. The electrons so produced have sufficient energy, say about 100 ev and these in turn ionise many more molecules. These ionisations are easily detected by following the tracks in cloud-chambers. It takes about 30 ev to form an ion pair. A 1 mev particle penetrating a material will produce nearly 33000 ion pairs, and in addition innumerable excited molecules. In the secondary processes, the slow moving heavier particles are more powerful ionising agents than the lighter particles or high frequency radiations. A proton having the same high energy as an electron will produce about 10^3 times more ionisations. The difference with photochemical processes lies here. In photochemical reactions each quantum activates one molecule. But with ionising radiations, the number of molecules ionised is quite large. 1 mev electron would ionise one molecule per 5000 molecules whereas 1 mev proton would ionise at least fifty per cent of the molecules it traverses. A quantitative measure of the radiation effects is given by what is known as the *G-value* of the reaction. It is defined as

$$G = \frac{\text{number of molecules reacting}}{100 \text{ ev of energy introduced}}$$

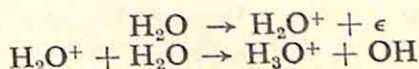
As already mentioned, the secondary processes are quite complex. Apart from the ions, excited molecules are also formed and, in fact, several excited states of the molecules are often reached. One of the secondary processes would be neutralisation of the ions yielding excited molecules. We thus have, with high energy appli-



The excited molecules A^* may next undergo complicated secondary transformations like

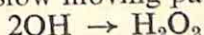


The irradiation of water, studied in some details, shows that the main transformations are



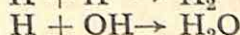
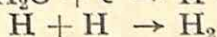
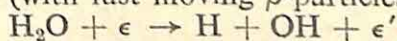
This may then follow different paths depending on the nature of ionising particle used :

(with slow moving particles)



or

(with fast moving β -particles)



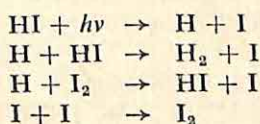
Investigations, with high energy radiations, on polymers had been of utmost importance in recent years. Polymeric substances on irradiation yield products with new properties and often with higher molecular weights. Polyethylenes, on irradiation, develop cross-links and produce materials of greater rigidity and higher melting point. There is unmistakable evidence of formation of free radicals on application of high energy radiations in such cases.

References for further reading

1. The photochemistry of gases—Noyes and Leighton
2. Fluorescence and phosphorescence—Pringsheim
3. Photochemistry and mechanism of chemical reactions—Rollefson and Burton
4. Radiation chemistry, J. Chem. Ed. 28, 404, (1951)—Burton

Problems

1. 5% of the energy of a 200-watt incandescent lamp emits visible light ($\lambda = 6000 \text{ \AA}$), how many quanta of the light is emitted per second. (Ans : 3×10^{19})
2. The bond dissociation energy of H-Br is 87 Kcals/mole. What is the kinetic energy of the H-atom produced by photodissociation of HBr with radiation of wave length $2537 \text{ \AA}$? (The Br atom is in ground state). (Ans : 25 Kcals/mole)
3. For the photodecomposition of hydrogen iodide, the mechanism suggested is

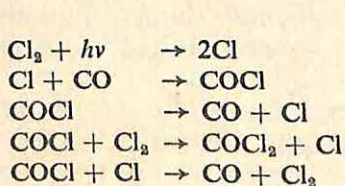


Rate
 I_a
 k_2
 k_3

Show that

$$\frac{dC_{I_2}}{dt} = \frac{I_a}{1 + k \cdot C_{I_2}/C_{HI}}$$

4. The formation of phosgene follows the mechanism



Rate

I_{abs}
 k_1
 k_2
 k_3
 k_4

Show that

$$\frac{dC_{COCl_2}}{dt} = k \cdot I_{abs}^{\frac{1}{2}} \cdot C_{Cl_2} \cdot C_{CO}^{\frac{1}{2}}$$

5. The photodecomposition of HI vapour was carried out with $\lambda = 2070 \text{ \AA}$ radiation. Absorption of each calorie of energy gave 1.44×10^{-5} gm of hydrogen. What is the quantum yield?

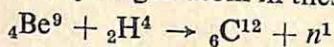
(Ans : 2)

NUCLEAR CHEMISTRY

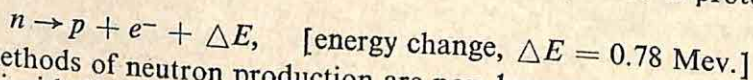
We have seen previously that three fundamental particles—protons, neutrons and electrons—constitute an atom. Of these the first two are contained in the nucleus and the last one exists in the extranuclear region. Ordinary chemical reactions we have so far considered involve processes in which only the electrons of the atoms take part, the nuclei of the participating atoms remain unaffected. From the beginning of this century a number of transformations were observed which are associated with changes in the nucleus of the atom. These indeed are nuclear reactions; many of these occur spontaneously in nature while others are artificially effected in the laboratory. In fact, since the second world war, the study of the nuclear reactions has developed into the new branch of “nuclear chemistry” with its own discipline.

The nuclear reactions may broadly be classified into three categories : (i) *Natural radioactivity* in which nuclei of heavy atoms spontaneously disintegrate with emission of radiations, (ii) *Artificial transmutation* of elements by bombarding the nuclei with energised particles, such as neutrons, (iii) *Artificial radioactivity* induced in normal light and non-radioactive atoms. A very brief outline of these phenomena will be given in this chapter.

Before considering the different types of nuclear changes, it would be convenient to make an acquaintance at first with the various kinds of fundamental *transient* particles that have been detected in the atom. In Chapter V, we have discussed the characteristics of protons, electrons and neutrons. The existence of neutrons was predicted earlier but the experimental confirmation came much later. Bothe and Becker (1930) and Curie-Joliot (1932) detected a penetrating radiation formed when certain light nuclei, like those of beryllium, were bombarded with α -particles. These radiations were uncharged but had high ionising power. It was James Chadwick who solved the problem by suggesting the existence of uncharged particles of mass equal to that of a hydrogen atom in these radiations ;



where n^1 refers to the uncharged particle. These particles were given the name “neutron”. We now know that this is an essential nuclear constituent. The neutron has a short life, its half-life period is 12.8 min. It decays into a proton and an electron,



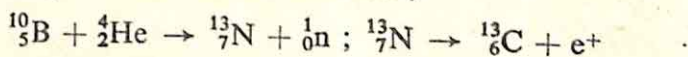
Other methods of neutron production are now known, such as bombardment of light nuclei with deuterons, or from nuclear fission in atomic reactor, etc.

XVIII.1. In addition to the above mentioned particles, there have been discovered a host of other sub-atomic particles of varying life times. The patterns of their discovery have mostly been the same viz. the impingement of high velocity particles on suitable target nucleus followed by critical analyses of the tracks in the cloud chamber, bubble chamber or in photographic emulsion. The high velocity projectiles have either been natural such as cosmic ray particles or the artificially accelerated ones.* Most of their discoveries have been accidental, though in many cases, their existence was predicted on the basis of the antiparticle theory of Dirac or meson field theory of nuclear forces due to Yukawa.

Antiparticles. Dirac, from his quanta mechanical theory of electrons, predicted the existence of an antielectron (later named positron) with a mass equal to that of an electron, but with a unit positive charge. Dirac's theory also provided equations for the existence of other antiparticles viz. antiprotons and antineutrons.

*Nuclear physicists use different types of particle accelerators such as cyclotron, synchrotron, betatron, linear accelerators.

At the beginning, such predictions were met with a storm of criticism from the theoretical physicists. Their doubts were, however, set at rest by Anderson's discovery of positron in 1932. Bombarding targets of boron, aluminium, etc. with α -rays, emission of positrons can be observed ;

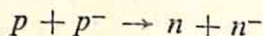


If a positron and an electron encounter, annihilation of both occurs with the production of two γ -ray photons ;



The positron is thus the antiparticle of the electron.

Later in 1955, antiproton [mass equal to that of a proton but with a unit negative charge] was discovered by Chamberlain, Segre, Weigland and others. In late fifties the existence of antineutrons was also proved. Antineutron differs from neutron in the sign of spin only. In fact, it has been demonstrated that when a proton strikes an antiproton, there would be a neutron and an antineutron :



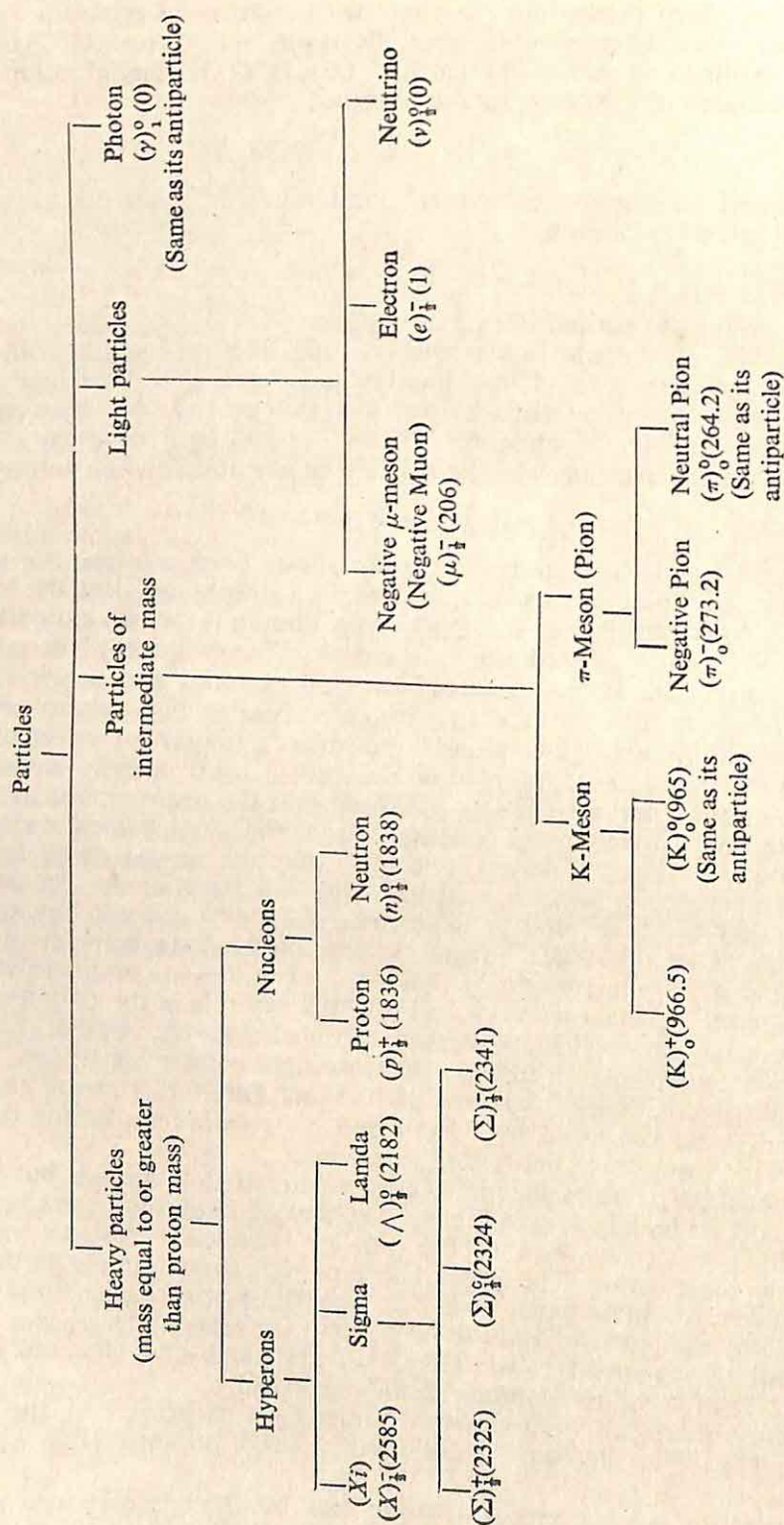
Each particle so far discovered has its antiparticle. Even photon, the unit of electromagnetic radiation, has its antiparticle, viz., antiphoton. But the two are experimentally indistinguishable. In other words, photon is its own antiparticle.

In 1935, Yukawa suggested the existence of "heavy quanta" in order to explain the 'short range attractive force' between neutrons and protons within the nucleus. This was in analogy with photons appearing in the electromagnetic field associated with long range Coulombian inverse square force between charged particles. The electromagnetic interaction between charged particles takes place through the photons. Similarly, it was proposed that the nuclear particles would also interact through some sort of 'quanta'. From the mathematical analysis of the appropriate equations, Yukawa concluded that the intermediates involved in the interaction of the nuclear particles could not be photons but particles having mass nearly 200 times that of an electron and carrying a unit charge positive or negative. These particles having masses intermediate between those of an electron and a proton are named "mesons". The mesons originate in close collisions between the nuclear particles and play the key-role in the stability of the nucleus. Two years later in 1937, Anderson and Neddermeyer, confirmed experimentally the existence of meson type particles through cosmic ray studies. These are μ -mesons, having half-life of the order of 10^{-6} sec. Later other meson particles called pi-mesons were produced by Powell and his co-workers having half-life of the order of 10^{-8} sec, which decay into μ -mesons.

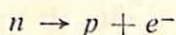
Other subnuclear particles having masses greater than π -mesons but lighter than neutrons, others having masses higher than that of a neutron have since been discovered. The present situation of the various subnuclear particles may be summed up as in table below. The mass of each particle is given in the paranthesis on the basis of electron mass equal to 1. The right superscripts indicate the nature of charge borne by the particles and the subscripts their magnitudes of spin. Antiparticles are not shown in the table. They exist and their characteristics can be guessed from that of the corresponding particles enlisted.

In this table, Muon has been classified under light particles from the standpoint of spin. The other medium weight particles have all spin value equal to zero.

The necessity for the concept of neutrino may be briefly mentioned here. A free neutron decays rapidly into a proton and an electron involving a disappearance of a mass equivalent to 1.5 electron mass. This should, therefore, be manifested in the kinetic energies of the proton and the electron. But the decay products do not have so much of energy. Pauli postulated that an undetectable particle with zero rest mass is simultaneously formed in neutron decay. This particle, later named neutrino by Fermi, accounts for the discrepancies of kinetic energy. Fermi developed the idea of neutrino still further in the complete β -decay theory of naturally radioactive substances.



XVIII.2. Natural Radioactivity. We have seen, in Chapter V, that the elements having atomic weight greater than that of lead are all radioactive. The nuclei of these heavy elements spontaneously disintegrate with emission of radiations. The rays emitted consist of three types of radiations, α , β , and γ -rays. The properties and behaviour of these rays have been described previously. The α -particles are really doubly-charged helium nuclei containing two protons and two neutrons. The emission of α -particles naturally indicates that it is the nucleus of the radioactive atom which is involved in the radioactive disintegration. The ejection of β -particles, which are electrons, seems anomalous in view of the fact that the nucleus contains only protons and neutrons. That the electrons of the emitted β -rays do not originate from the outer extranuclear shells of the atom is obvious. For, when valence electrons come out, the atom is ionised which promptly picks up other electrons to revert to the original atom. But when a radioactive atom emits a β -particle, the product is a new atom and it does not revert to the original atom; the transformation is irreversible. The outgoing β -particle which leads to the change of an atom into another with a different atomic number cannot originate in the outer-shell. Although the β -particles do not pre-exist in the nucleus, these are created at the moment of their emission, due to the transformation of neutrons into protons through a complicated mechanism :



When an α - or a β -particle is emitted, the nucleus undertakes an energy rearrangement. Such a rearrangement within the nucleus may lead to a decrease in potential energy. The excess energy is then emitted in the form of γ -rays which are electromagnetic waves of very high frequency. γ -rays therefore often accompany α - or β -ray emissions.

In 1903, Rutherford and Soddy proposed that the nuclei of very heavy elements (having atomic numbers greater than 82) are unstable and these decompose spontaneously emitting an α or a β particle. This leads to the formation of a new element with different physical or chemical properties. The product of radioactive disintegration may itself be radioactive and undergo further disintegration. Thus a genetic series of radioactive elements occur; the process continues until a stable nucleus of lead or one of its isotopes is formed. We have seen (Chapter V), three such consecutive radioactive series, all ultimately ending in an isotope of lead. We shall presently come across another series—Neptunium series—which has been obtained from elements created through artificial transmutation.

The radioactivity of an element is independent of temperature and physical condition and environment. It is also unaffected by chemical combination with other elements. The energy associated with radioactive disintegration is of the order of 10^9 calories per mole whereas in a chemical reaction it is of the order of 10^5 cal per mole.

The expulsion of α - or β -particles from the nucleus causes a change in the nuclear charge and hence the atomic number changes. The different members of a radioactive series will have atomic numbers different from their immediate predecessor. Hence, these would occupy different positions in the periodic table which is summarised in "Group displacement law" of Fajans, Soddy and Russel. According to this, "When an atom loses an α -particle its atomic number diminishes by two units; the daughter element has an atomic weight less by four units than that of its mother and is shifted in the periodic table two places to the left of its mother. Again, when the radioactive atom emits a β -particle, the daughter element has the same atomic weight but its atomic number increases by one unit; its position is shifted in the periodic table by one place to the right of its mother." The successive expulsion of an α -particle and two β -particles brings the original element back to its original position in the periodic table with the same atomic number but its atomic weight is four units less. (see sec. V.10).

The rate of radioactive disintegration of an element at any instant of time is proportional to the number of atoms (n) present; i.e.,

$$-dn/dt = \lambda n$$

where λ is the rate constant or disintegration constant and is characteristic of the given element. The radioactive changes therefore follow the first order equation.

Integrating between $t = 0$ and $t = t$, we have, $\lambda = \frac{1}{t} \ln \frac{n_0}{n}$, where n_0 is the number of radioactive atoms initially present.

In the exponential form, the relation would be, $n = n_0 e^{-\lambda t}$. The half-life of a radio element would be given by,

$$t_{\frac{1}{2}} = \frac{1}{\lambda} \ln \frac{n_0}{n_0/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} = \text{constant} \quad \dots \text{(XVIII.2)}$$

The time required for 50% decomposition is thus independent of the initial amount and is specific for a given element. The half-life may be as high as 10^9 years or it may be as small as 10^{-6} sec.

Suppose a radioactive element (A) disintegrates to produce the daughter element (B), which is also radioactive. Suppose also λ_A and λ_B are the rate constants of disintegration of A and B. The rate of decay of each of these will be governed by eqn. XVIII.1. If n_A be the number of atoms of A at any time, then the rate at which B is produced is $n_A \lambda_A$. The rate at which B disintegrates is $n_B \lambda_B$, where n_B is the number of B atoms present. When the 'steady state', commonly called radioactive equilibrium, is attained, the rate of formation of B and its disintegration rate would be the same; i.e.,

$$n_A \lambda_A = n_B \lambda_B$$

$$\text{Hence} \quad n_A/n_B = \lambda_B/\lambda_A = t_{\frac{1}{2}(A)}/t_{\frac{1}{2}(B)} \quad \dots \text{(XVIII.3)}$$

Allowing sufficient time, the equilibria in a radioactive series is given by,

$$n_A \lambda_A = n_B \lambda_B = n_C \lambda_C = n_D \lambda_D = \dots$$

The radioactivity of an element is expressed in units of 'curie' (c). A curie is defined as the quantity of the radioactive material in which 3.70×10^{10} disintegrations occur per second. The smaller unit is the 'microcurie' (μc) having 3.70×10^4 disintegrations per second. The number of atoms present in 1 curie is then $(3.7 \times 10^{10})/\lambda$.

Problem. The half-life of ^{232}Th is 1.4×10^{10} years and that of its daughter element ^{228}Ra is 7 years. What is the weight of ^{228}Ra in equilibrium with 1 gm of ^{232}Th ?

Let w be the wt. of ^{228}Ra in equilibrium.

We know,

$$\frac{n_{\text{Th}}}{n_{\text{Ra}}} = \frac{t_{\frac{1}{2}}(\text{Th})}{t_{\frac{1}{2}}(\text{Ra})}$$

$$\therefore \frac{N_0/232}{w.N_0/228} = \frac{1.4 \times 10^{10}}{7} = 2 \times 10^9 \quad (N_0, \text{Avogadro number})$$

or

$$w = 228/(232 \times 2 \times 10^9) = 5 \times 10^{-10} \text{ gms}$$

Problem. Natural potassium contains ^{40}K in the proportion of 120 p.p.m. and the total potassium content in sea water is given by 400 p.p.m. Calculate the specific radioactivity of sea water due to ^{40}K per c.c., if half-life of ^{40}K is 1.2×10^9 years.

$$\text{The rate constant } \lambda = \frac{0.693}{t_{\frac{1}{2}}}$$

$$\text{The number of } ^{40}\text{K} \text{ present in a curie, } n = \frac{3.7 \times 10^{10}}{\lambda}$$

$$\text{The weight of } ^{40}\text{K} \text{ in a curie, } w = n \times \frac{40}{N_0} \quad (N_0, \text{Avogadro number}).$$

$$\begin{aligned} \text{or} \quad w &= \frac{n \times 40}{N_0} = \frac{3.7 \times 10^{10}}{\lambda N_0} \times 40 = \frac{3.7 \times 10^{10} \times 40 \times t_{\frac{1}{2}}}{N_0 \times 0.693} \\ &= \frac{3.7 \times 10^{10} \times 40 \times 1.2 \times 10^9 \times 365 \times 24 \times 3600}{6.02 \times 10^{23} \times 0.693} = 1.35 \times 10^6 \text{ gms} \end{aligned}$$

$$\therefore \text{Radioactivity of } ^{40}\text{K per gm} = \frac{1}{1.35 \times 10^8} = 7.4 \times 10^{-8} \text{ curie}$$

Again, 10 gms of sea-water contains 400 gms of potassium.

Assuming density of sea-water as 1, we find

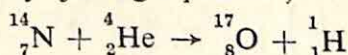
1 c.c. of sea water contains 4×10^{-4} gms of potassium.

But potassium has ^{40}K content of 1.2×10^{-4}

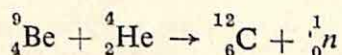
Hence amount of ^{40}K present per c.c. of sea water is $(4 \times 10^{-4}) \times (1.2 \times 10^{-4}) = 4.8 \times 10^{-8}$ gms.

$$\begin{aligned} \text{The radioactivity of the same} &= (4.8 \times 10^{-8}) (7.4 \times 10^{-8}) \text{ curie} \\ &= 3.55 \times 10^{-15} \text{ curie} = 3.55 \times 10^{-7} \mu\text{c. per c.c.} \end{aligned}$$

XVIII.3. Artificial Transmutation of Elements. The process of natural splitting of heavy nuclides accompanied by emission of radiations urged the scientists to find ways for the artificial disintegration of the naturally stable elements. The first act of disintegration of the stable element, nitrogen, by α -particle bombardment is generally attributed to Rutherford (1919), although some doubts have been cast on Rutherford's original claims. It was however definitely established that when nitrogen is struck with α -particles, a nuclear reaction takes place producing oxygen and simultaneously ejecting a proton ;



Similarly,



(As usual, symbols are proton ${}^1_1\text{H}$, neutron ${}^1_0\text{n}$; α -particle ${}^4_2\text{He}$, etc.)

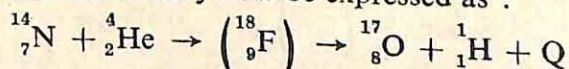
Bombardment of target nucleus with projectiles may be divided into three categories :

(i) *Elastic Scattering* in which the identity of the particles as well as their combined kinetic energy remain unaltered before and after the collision.

(ii) *Inelastic scattering* where the outgoing particles are the same as the incident ones but there would be some loss of their energy.

(iii) *Nuclear transformations*, the outgoing particles are different from the incident ones. It is with this type of changes we are interested here.

It was suggested by Böhr in 1936 that the nuclear reactions would involve two-stage processes. A compound nucleus comprising the projectile and the target nucleus is first formed. This has a life-time too short to be measured ($\sim 10^{-17}$ sec) but long enough compared to the time of transit of the projectile across the largest nucleus ($\sim 10^{-21}$ sec). The compound nucleus subsequently splits down to new products in ways which are energetically feasible. The atomic number of the compound nucleus must be the sum of the atomic numbers of the target nucleus and the projectile. The compound nucleus would therefore represent an isotope of the element which has the "added" value as atomic number. The transmutation of nitrogen, mentioned earlier may now be expressed as :



The compound nucleus is that of a fluorine isotope having atomic number $7+2=9$. The mass number of the compound nucleus is the sum of the mass numbers of the initial particles, and also the sum of the mass numbers of the final products. The constancy of mass numbers is true but the total atomic masses would not remain constant, for atomic masses are slightly different from mass numbers. When the total atomic mass of the products is less than that of the initial participants, an energy Q will be given out, governed by the relation, $mc^2 = \epsilon$. The value of Q will be negative i.e., energy will be absorbed when the total mass of the products is more than that of the initial reactants. The value of Q in the transmutation cited above may be computed as follows :

Initial participants	
${}^{14}\text{N}$	= 14.00755
${}^4\text{He}$	= 4.00388
	18.01143

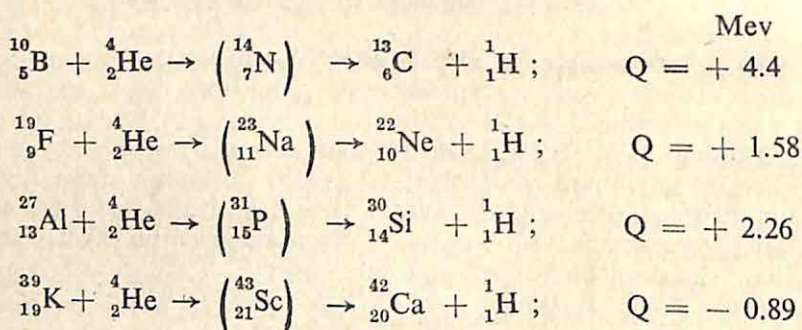
final products	
${}^1\text{H}$	= 1.00815
${}^{17}\text{O}$	= 17.00453
	18.01268

$$\Delta m = 0.00125 \text{ amu} = 0.00125 \times 931.2 = 1.16 \text{ Mev.}$$

(1 amu = 931.2 Mev) ; since there is an increase in mass, $Q = -1.16 \text{ Mev.}$

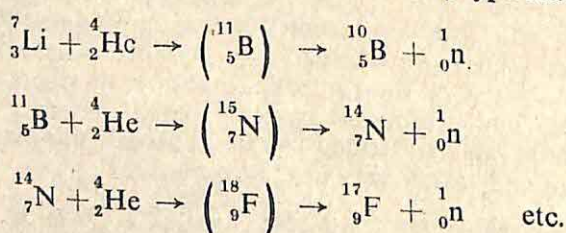
This corresponds satisfactorily to experimental measurements of kinetic energies.

For brevity, the nature of nuclear reactions is indicated by writing the projectile and the ejected particle within a paranthesis, thus, in the example cited above, the projectile is an α -particle and the emitted particle is a proton, hence this is an (α, p) type reaction. We may mention here some other (α, p) reactions, as,

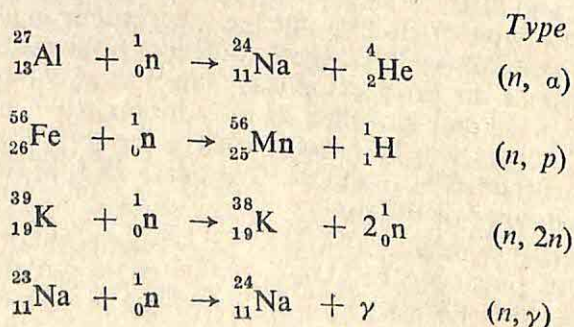


There are various other artificial transmutations carried out in which missiles other than α -particles are used, such as (i) neutrons (ii) protons (iii) deuterons (iv) γ -rays. In these nuclear reactions (excluding fission type reactions), when bombardment energy is in the range 0–10 Mev, γ -rays, protons, neutrons and α -particles may be ejected. At higher bombardment energies, 10–25 Mev, two neutrons or sometimes a proton and a neutron together are ejected. Very high-energy projectiles (100–400 Mev) cause *spallation*, i.e., an event in which many nucleons and groups are simultaneously given out.

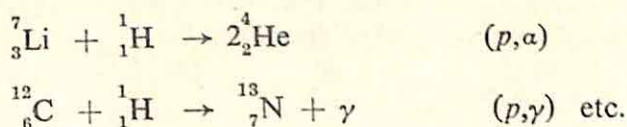
As would be expected neutrons provide the most effective means of disintegrating a stable nucleus. The α -particles because of their charge-content are not as efficient as others. Deuterons, in some cases, act as very efficient projectiles for transmutations. The (d, p) type transmutations are believed to proceed by stripping mechanism and do not require the formation of the intermediate compound nucleus postulated by Bohr. Examples of different types of nuclear reactions with different missiles are given below. Some of the (α, n) type reactions are :



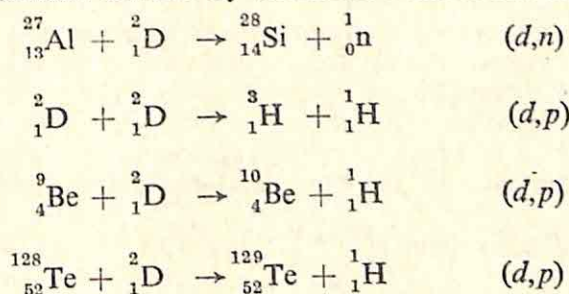
Nuclear reactions effected with neutron bombardment may lead to ejection of different particles, as illustrated below :



Examples of disintegration by protons are :



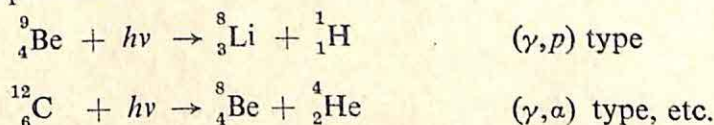
Some reactions induced by accelerated deuterons are :



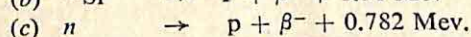
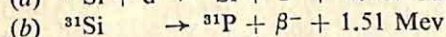
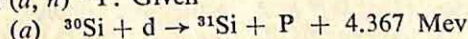
The last two reactions are believed to proceed by stripping mechanism, *i.e.*, the projectile deuteron, while approaching the target nucleus, is stripped of a proton due to intense repulsion and the residual neutron finds easy access into the target nucleus.

Stable nuclei have also been disintegrated using high energy γ -ray photons (or X-ray photons of high energy). This is indeed a case of *photodisintegration*. The emitted particles may be neutron, proton, α -particles etc. A very interesting example is ${}^1_1\text{H} + h\nu \rightarrow {}^1_1\text{H} + {}^1_0\text{n}$ (γ, n) type. Since the masses of proton and deuteron are accurately known from mass spectrograph data, this reaction provides an accurate method of determination of neutron mass, 1.008987.

Other examples are :

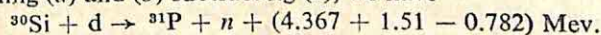


Problem. Calculate the Q value for the formation of ${}^{31}\text{P}$ in the ground state in the reaction, ${}^{30}\text{Si} (d, n) {}^{31}\text{P}$. Given



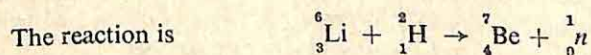
The reaction proposed is ${}^{30}\text{Si} + d \rightarrow {}^{31}\text{P} + n + Q$.

Adding (a) and (b) subtracting (c), we have



Hence $Q = 5.095 \text{ Mev.}$

Problem. The Q value of ${}^6\text{Li} (d, n) {}^7\text{Be}$ reaction is 3.40 Mev. Determine the atomic mass of ${}^7\text{Be}$.



Let the atomic mass of ${}^7\text{Be}$ be x , then accepting standard values of other atomic masses,

Initial particles

${}^6\text{Li} = 6.01697$

${}^2\text{H} = 2.01474$

Final Particles

${}^7\text{Be} = x$

$n = 1.00899$

$$\therefore \text{Loss in mass } \Delta m = (6.01697 + 2.01474 - 1.00899 - x) = (7.02272 - x)$$

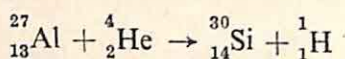
$$\therefore Q = (7.02272 - x) \times 931.2 \text{ Mev.}$$

i.e., $3.40 = (7.02272 - x) \times 931.2$

whence $x = 7.01907$

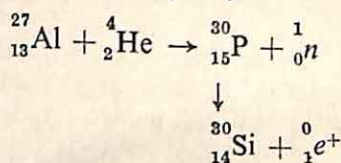
XVIII.4. Artificial Radioactivity. The artificial production of elements possessing radioactivity had its beginning in the experiments of Frederik Joliot and

Irene Joliot-Curie while studying the effect of α -impingement on metallic aluminium. The artificial disintegration of aluminium by α -particles leads to the production of silicon accompanied by proton emission.

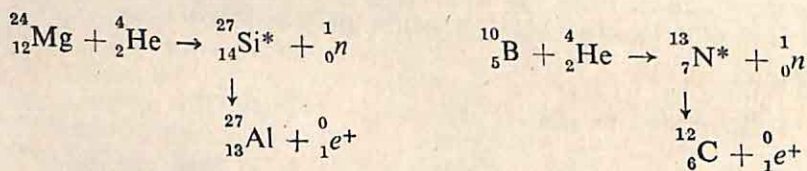


It was found by the Joliot couple that in addition to proton emission, this disintegration is also accompanied with neutron and positron emission and that while proton and neutron emission ceased as soon as α -irradiation was stopped, the positrons continued to be emitted. An immediate explanation for the phenomenon was offered. The artificial disintegration of aluminium by α -particles proceeds in two ways, one of which follows the pattern shown above. In another way, α -bombardment first produces an unstable isotope of phosphorus with the ejection of a neutron. This unstable phosphorus nucleus is radioactive and decays into

silicon with the emission of a positron, $({}_1^0e^+)$.



This was the first instance of the discovery of induced radioactivity where a stable non-radioactive nucleus after transmutation was rendered radioactive. This was soon followed by a spate of discoveries of other artificially produced radioactive isotopes such as,

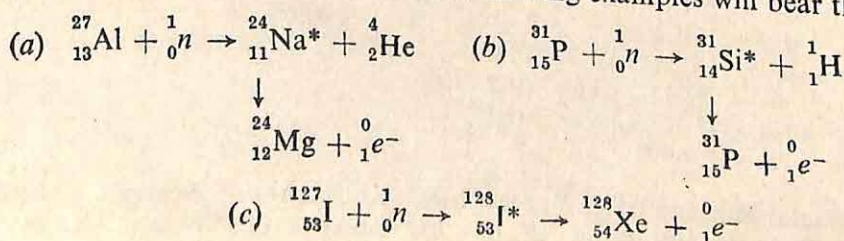


The artificial radioactive elements behave in the same fashion as the naturally radioactive ones. The decay of these elements follows the same first order law and each of these created radioactive elements has its own half-life period.

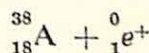
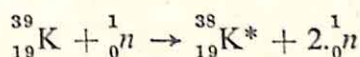
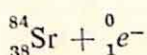
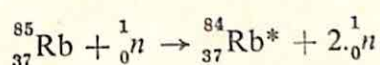
The examples cited above constitute cases where the impinging projectiles were α -particles. These are effective with relatively light elements and find it increasingly difficult to penetrate into nuclei of heavier elements because of intense electrical repulsions. Fermi started using neutron irradiation of different elements to obtain radioactive isotopes. He soon found this method as the most convenient for obtaining the radioactive isotope of almost any element. The electron shells of the target atom do not offer much opposition to the neutral neutrons which can easily reach the nucleus.

There is an essential difference in the production of radioactive isotopes by α -bombardment and by neutron-bombardment. In the former case, (i) the generation of radioactive isotopes is simultaneously accompanied by ejection of neutrons and (ii) the radioactive species formed are all positron-ray active.

In the neutron-irradiation cases (i) α -emissions, proton emissions or a complete capture of neutrons occur when the radioactive species are formed and that (ii) the latter are electron emitters. The following examples will bear this out :

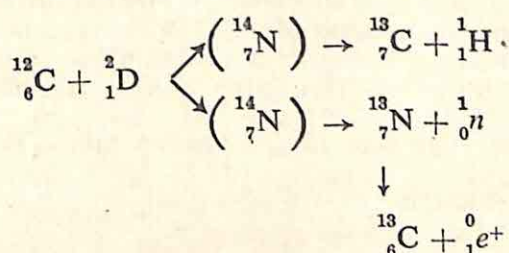


There is, however, an additional class of neutron irradiation in which the radioactive isotopes result from $(n, 2n)$ process and the radioactive species may be positron or electron emitters.

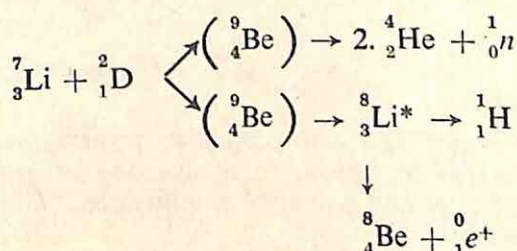


Artificially accelerated particles like protons, deuterons can bring about disintegration of nuclei in which the initial products are radioactive. The disintegrations involving (d, α) , (d, p) and (d, n) generally lead to radioactive species which are either positron or electron emitters.

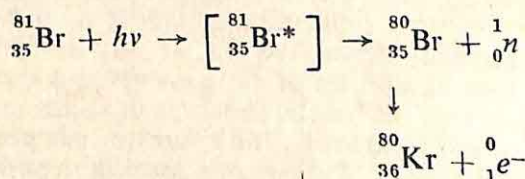
To illustrate : (i) Carbon bombarded by deuterons follows two paths :



(ii) Lithium (${}^7\text{Li}$) bombarded by deuteron also follows two paths :

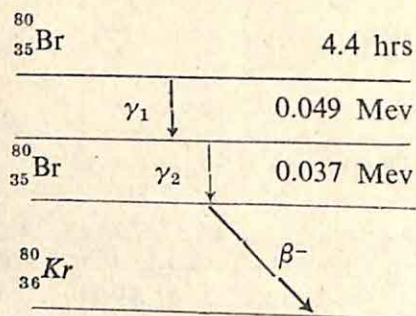


Irradiation with γ -rays may also lead to the production of artificial radioactive atoms, for example, when bromine is bombarded with γ -rays following changes occur :

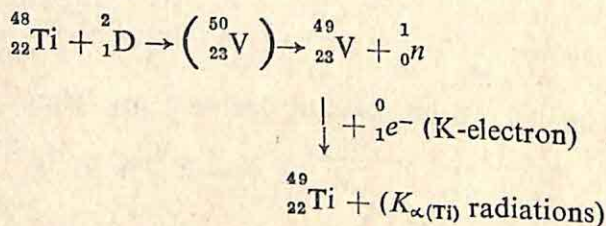


It is now well-known that many of the nuclei produced by transmutation remain in an excited state or *metastable state*. The metastable species then parts with the excess energy and passes to the ground state by emitting one or more γ -rays. The nucleus in the metastable and in the ground state has the same atomic mass number and charge but the energy content is different in the two states. These are called *nuclear isomers*. After the emission of γ -ray, the nucleus suffers the radioactive disintegration and is transformed into a new one. A very interesting example is found in bromine. After irradiation, ${}_{35}^{80}\text{Br}$ is formed in a highly energised state and it has a half-life of 4.4 hrs. Two γ -rays are emitted from it in cascade

when the nucleus passes into the ground state. Its half-life is then found to be 18 min. $^{80}_{35}\text{Br}$ then exhibits induced activity by emitting a β -particle.



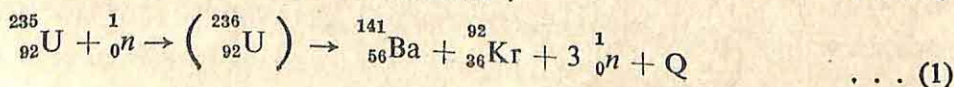
Some irradiation mechanisms are explained by what is known as *K-capture*. In such cases, the nucleus formed by transmutation picks up an electron to revert back to an isotope of the original parent atom. The electron is taken up by the nucleus usually from the nearest K-shell; a proton thus becomes a neutron, atomic number decreasing by unity. The filling of the vacancy in the K-shell leads to emission of X-rays. The case of $^{49}_{23}\text{V}$ passing into $^{49}_{22}\text{Ti}$ by capturing a K-electron is a well-known example.



XVIII.5. Nuclear Fission. Apart from the nuclear transformations in natural radioactivity and in artificial disintegration, there are two other types of nuclear reactions of profound theoretical and practical significance. These are (i) Nuclear fission and (ii) Nuclear fusion.

Nuclear fission. In 1934, Fermi and his collaborators were engaged in studying neutron-induced radioactivity on heavy atoms with the object of producing, by transmutation, some transuranic elements, elements having atomic numbers higher than 92 (Sec XVIII). They observed that uranium on being bombarded with neutrons yielded products which show several different types of strong β -ray activity. Although two of the β -ray emissions could be interpreted on the basis of formation of a transuranic element, the activity of other emissions could not at the time be satisfactorily accounted for. It was in 1939 Otto Hahn and S. Strassmann, from a very careful set of experiments and the analysis of the results of the same, established that one of the products of neutron irradiation of uranium was an isotope of Barium (at no. 56). The other nucleus produced was thus considered to be krypton (at. no. 36). This was an astounding observation. Before this, all the transmutations known—natural and artificial—involved small changes in mass or atomic numbers; in those changes either there was an increment in mass by absorption of a particle or there would be a decrease due to emission of a particle. It was the first instance of a major rupture of a heavy nucleus into fragments having atomic masses of medium sizes. Such disintegrations in which a heavy nucleus breaks up into two nuclei of comparable masses are called 'nuclear fissions'.

Further probe into the splitting of uranium by neutron bombardment revealed that among the different isotopes of uranium, it was ^{235}U which was most readily fissionable. The rupture takes place as follows :



Careful experimental observations have brought out a number of facts which, shorn of details, may be summarised below.

(a) In the process of nuclear fission a large amount of energy is released which is considerably greater than that evolved in any other process. The number of nucleons before and after the process remains the same, but the sum of the mass of the fragments and released neutrons is less than the mass of the disintegrating U-atom and the projectile neutron. An approximate calculation, with Einstein's equation $\epsilon = mc^2$, in the above process shows that there would be a mass defect of about 0.215 amu which is equivalent to about 200 Mev. This indeed is a very large quantity of energy. It became immediately evident that such fission would be a source of enormous power.

(b) Fission of each uranium nucleus is accompanied by release of 2~3 neutrons. These neutrons, under suitable conditions, bombard fresh uranium atoms splitting them and producing more neutrons. Thus a chain reaction of splitting would ensue and its propagation would rapidly increase. At each step considerable energy would be released. This may be broadly represented as Fig. XVIII.1.

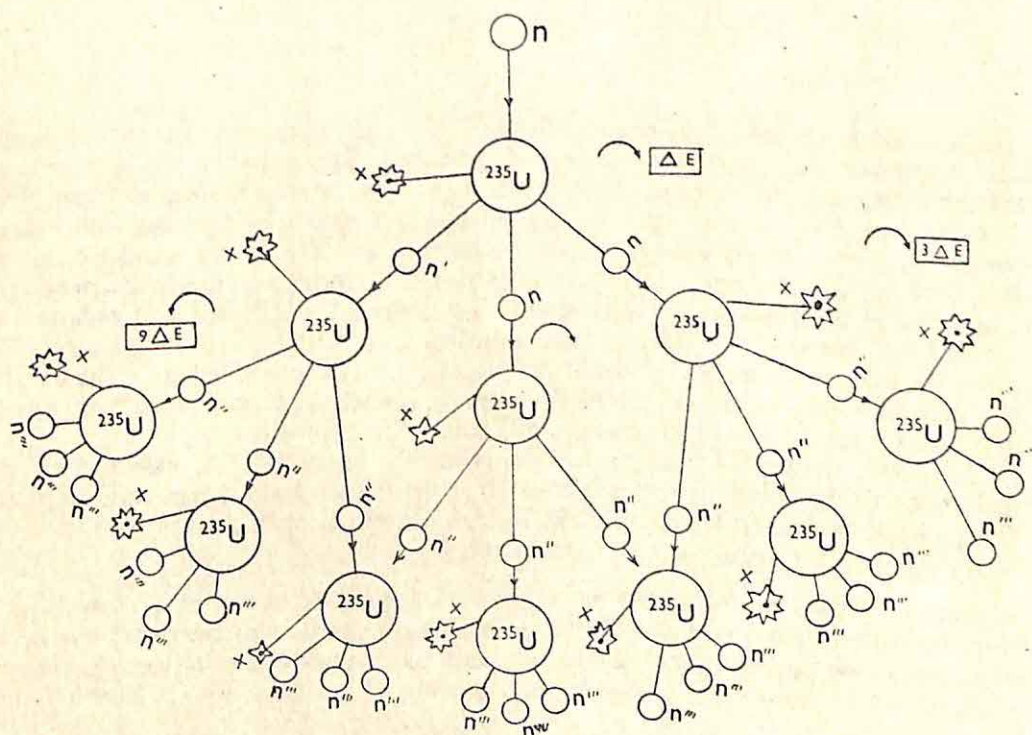
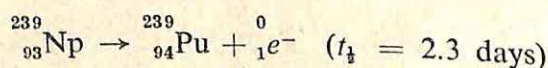
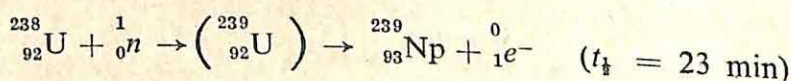


FIG. XVIII.1 Schematic representation of chain reaction in fission. ($n, n', \dots$ neutrons), stars (X) indicate fission products.

(c) ^{235}U undergoes fission both by fast as well as slow neutrons, though the latter are more effective in carrying out the rupture. The main isotope ^{238}U , in general, absorbs slow neutrons but instead of undergoing fission, it yields transuranic elements (Np and Pu) as follows.



... (II)

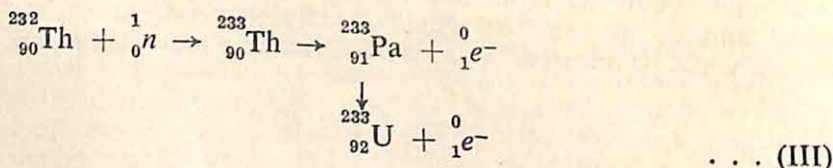
That is, with slow neutron bombardment, ^{238}U is first transformed into the element ($Z = 93$) called neptunium. This is radioactive and spontaneously disintegrates into the next element plutonium ($Z = 94$) with β -ray emission.

With fast neutrons, ^{238}U suffers nuclear fission to a small extent. In the fission of ^{235}U , the fragments produced are unsymmetrical, i.e., the product

nuclei differ in mass numbers by a large margin. The fission of ^{235}U is more symmetrical. During the fission of ^{235}U , the elements formed as fragments belong to two groups, one having mass numbers near 140 and the other near about 95.

(d) Plutonium formed from uranium by β -emissions (see II above) is fissionable like ^{235}U . It has comparatively a long half-life period and can thus be stored in quantities. The isotope ^{235}U occurs in low amounts in uranium minerals [$^{238}\text{U}/^{235}\text{U} = 140$], and its separation from the abundant isotope ^{238}U is rather hard. Plutonium has thus proved to be the chief source of atomic energy both for peaceful uses as well as for destructive purposes including the nuclear bomb.

(e) The isotope $^{233}_{92}\text{U}$ obtained from thorium by slow neutron irradiation also suffers nuclear fission like plutonium yielding considerable amounts of energy. The stages in its formation are :



XVIII.6. Atomic Bomb. On bombarding ^{235}U with neutrons, for every single fission approximately 200 Mev energy is released. The process yields moreover 3 new neutrons on an average, each in its turn leads to the fission of fresh ^{235}U . At every stage, in this way, the energy output will multiply and the cumulative effect of even one initial fission would be enormous. The chain would continue if the piece of ^{235}U taken is large enough and the secondary neutrons produced find targets. If the piece of ^{235}U is small, the neutrons produced will escape and the chains will break up. There is thus a limiting or critical size of the target for intense production of energy by chain propagation. If the size is below the critical limit, there will be no explosion and the process is safe. A larger piece from which the secondary neutrons cannot escape will cause the explosion.

It has been estimated that on the capture of a neutron by a fissile ^{235}U , the secondary neutrons are expelled in about 10^{-14} sec. And the average time required for the capture of a secondary neutron by the target nuclei is about 10^{-8} sec. We can now attempt an approximate calculation.

Suppose we have 1 Kg of pure ^{235}U , exposed to neutron bombardment. Consider only 1 neutron starts the initial fission of one ^{235}U nucleus. Let us further assume each fission yields 3 neutrons on an average, though it may be somewhat less. Suppose that the chain propagates to x steps, then the total number of fission occurring, due to one initial fission, is 3^x (c.f. Fig. XVIII.1). We know,

$$\text{number of } ^{235}\text{U} \text{ present per Kg} = \frac{6 \times 10^{23} \times 1000}{235} \approx 25 \times 10^{23}.$$

If all the atoms suffer fission, then $3^x = 25 \times 10^{23}$, whence $x \approx 51$. And this would happen in a period of 51×10^{-8} sec ; i.e., approximately a millionth of a second, hence the explosion.

The energy released per fission = 200 Mev.

$$= 200 \times 1.6 \times 10^{-6} \text{ ergs} = 3.2 \times 10^{-4} \text{ ergs.}$$

That is, the total output of energy from 1 Kg of ^{235}U is

$$25 \times 10^{23} \times 3.2 \times 10^{-4} \text{ ergs} = \frac{8.2 \times 10^{20}}{10^7} \text{ watt-sec} = \frac{8.2 \times 10^{20}}{10^7 \times 1000 \times 60 \times 60} = 2.2 \times 10^7 \text{ KWh.}$$

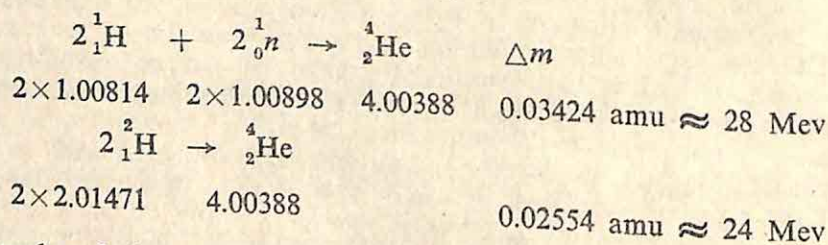
This energy appears within 10^{-6} sec as heat in the uranium from which the fission products cannot escape. It produces a tremendous explosion resulting into a violent blast and an intense temperature of 10^7°K , associated with dangerous radioactivity. It is necessary that ^{235}U should be pure. The presence of ^{238}U or other materials will absorb the neutrons and break the chain.

In fact, in the actual operation two rods of ^{235}U , each below the critical size, are taken and at the desired moment the two pieces are brought together to exceed

moderator should therefore be present in sufficient quantity and properly distributed between the uranium rods so that all neutrons may be thermalised. These thermal neutrons will then be used for causing fission of more ^{235}U and some will be captured by ^{238}U to produce nuclides. The moderators chosen are substances containing atoms of low atomic weight e.g., H, He, Li, Be, and carbon. Considering other factors, carbon has been found to be quite suitable as moderator. Deuteron in the form of heavy water is also used as moderator in some type of reactors.

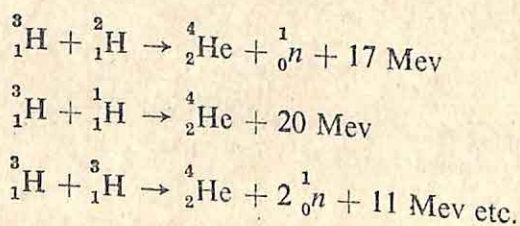
The total uranium taken must exceed the critical size in order to allow the chain reaction to proceed. But the same is controlled by inserting in between the uranium rods sheets or blocks of substances like cadmium or boron-steel which absorb the neutrons. These rods can be moved in or out. In order to slow down the output of power, these are pushed in, or when more reaction is sought these are partially withdrawn. The energy produced as heat is removed from the reaction by a stream of CO_2 to a suitable boiler.

XVIII.8. Nuclear Fusion. The energy released in the fission of nuclei originates from the loss of mass occurring in the process. On the other hand, if very light nuclei could be joined or *fused* together, there would be a loss in mass. This can be easily understood from the packing fraction curve (Chapter V). For example if two protons and two neutrons would fuse, or if two deuterons would unite, the loss in mass would be Δs follows.



That means, such a fusion process would lead to liberation of energy. But the real difficulty in effecting such a fusion arises from the intense repulsion between the positive nuclei. If however the temperature could be raised very high the repulsion might be overcome by the increase in kinetic energy of the nuclei. Calculation shows that the temperature required would be of the order of $10^6 \sim 10^7^\circ\text{K}$. Such high temperatures can be attained terrestrially only in a fission reaction. Thus if plutonium or ^{235}U be allowed to undergo fission in an explosive chain reaction in an abundance of protons or other hydrogen isotopes, the temperature would be high enough to initiate fusion processes amongst the latter. The momentary high temperature would provide the nuclei of lighter elements with enough kinetic energy to penetrate into each other and fuse. Since very high temperature exists for a brief lapse of time, only such nuclear fusions which proceed with extraordinary rapidity can happen.

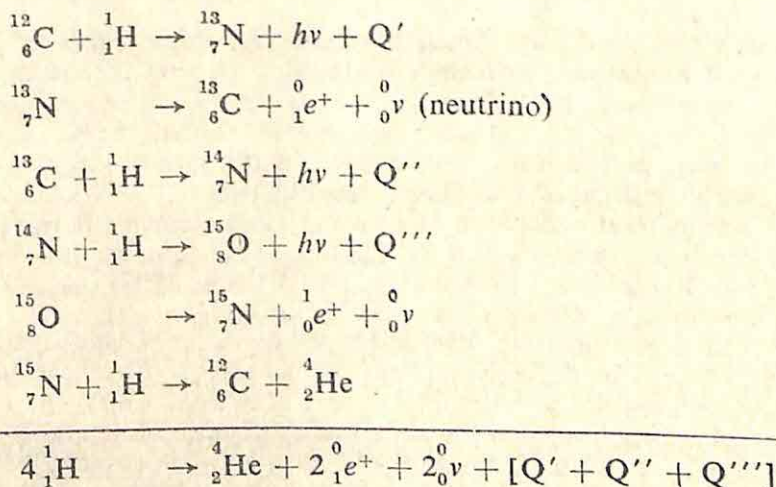
It is believed that such conditions have been attained in the creation of thermonuclear bombs, such as the *hydrogen bomb*. The exact fusion reactions for the hydrogen bomb have not been revealed, but it is generally thought the tritium and deuteron or proton are involved in the process. The transformation would be of the type :



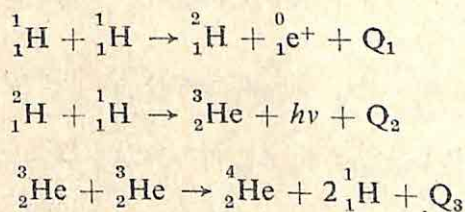
In the bomb, probably there is a small core of plutonium fission bomb to act as detonator. This is surrounded by thick cover of fusable material, which in turn is enclosed by natural uranium. The fast neutrons produced in fusion leads to the fission of the surrounding uranium. The fusion process is not governed by critical size limit, very large hydrogen bombs can therefore be produced. The results of the explosion of such devices are stupendous and frightening.

XVIII.9. Stellar Energy. The explanation of how the stars continuously emit such enormous amounts of energy for millions and millions of years is now available from our knowledge of nuclear reaction processes. The temperatures of the interior of the stars are exceedingly high. Our sun's interior has a temperature of the order of 10^7 °K. There are stars having much higher temperature ($T \sim 10^8$ °K). Such high temperatures were originally attained during their formation by contraction from gaseous nebulae. At such high temperatures, the atoms are completely stripped of their electrons and the bare nuclei must have very high thermal energies. There is hardly any doubt that fusion reactions, overcoming the repulsive forces, must be occurring at a high rate which is responsible for such colossal output of energy.

In 1938, Bethe and Weizsacker independently proposed that the real process of fusion was the formation of a ${}^4\text{He}$ nucleus from four protons, ${}^1\text{H}$, the latter being present in abundance in stellar bodies. It is a cyclic process carried through the intermediary ${}^{12}\text{C}$ and ${}^{14}\text{N}$ nuclei, in the following way :



i.e., four protons fused to yield a He-nucleus. Bethe showed that energy liberated in each cycle is about 28 Mev. It is now believed that in very hot stars, this cycle represents the energy emission. But in stars having somewhat lower temperature, such as our sun, an alternative mechanism seems to be more appropriate. This is a *proton-proton* cyclic process :



This indeed is a synthesis of helium nucleus from fusion of four protons, the energy output is about 25 Mev.

XVIII.10. The Transuranic Series. The possibility of synthesising elements with atomic numbers greater than that of uranium had been envisaged and three discoveries in the thirties of this century spurred the physicists on to the job of their syntheses. The first was the discovery of artificial radioactivity, the second was Anderson's discovery of neutron, a convenient projectile for nuclear bombardment and the third the cyclotron or particle accelerator devised by Lawrence. The details of the discoveries of the transuranic elements, the modes of their separation, their physical and chemical identification, each bearing testimony to human ingenuity and diligence, will be omitted here. Instead, only a brief resume covering

the salient aspects of their formation will be presented. Researches spanning over 21 years (1940-61) heralded the birth of eleven new elements with atomic numbers 93 to 103, all beyond Uranium. These are,

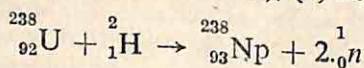
TRANSURANIC ELEMENTS					
Name	At. no.	atomic mass number	Name	At. no.	atomic mass number
Neptunium (Np)	93	231-241	Einsteinium (Es)	99	246-256
Plutonium (Pu)	94	232-243	Fermium (Fm)	100	250-256
Americium (Am)	95	237-244	Mendelevium (Md)	101	256* ~
Curium (Cm)	96	238-245	Nobelium (No)	102	251* ~
Berkelium (Bk)	97	243-245	Lawrencium (Lc)	103	*
Californium (Cf)	98	244-246			

(*range not definitely established)

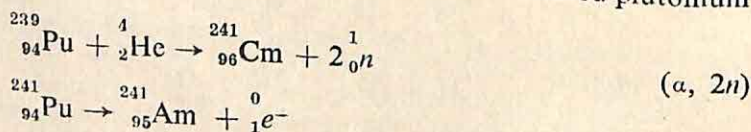
These elements do not occur naturally, although traces of plutonium have been detected in nature. Any such plutonium existing in nature is supposed to have been formed due to nuclear reaction set in by the impingement of suitable target nuclei by cosmic rays. It must be conceded that all the eleven elements, synthesised in 21 years period must have existed in the primordial creation of the earth but that all have decayed and disappeared by now.

The general procedure of creating these elements is by (i) neutron irradiation of some heavy nucleus and (ii) feeding some suitable nucleus of an element with positive charges, such as deuterons, α -particles, carbon or boron nuclei accelerated in a cyclotron or a hilac (heavy ion linear accelerator).

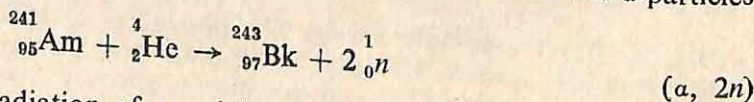
At the present time several dozens of isotopes of transuranic elements have been prepared by different techniques. In what follows, we shall usually confine to the process employed when it was first prepared. The neutron irradiation consists in bombarding uranium nucleus with suitable neutrons. We have already seen how this leads to the formation of the first two transuranic elements—neptunium and plutonium—by β -decays. These two elements can also be obtained by deuteron irradiation of ^{238}U (Seaborg, Mcmillan et al), ($d, 2n$) reaction.



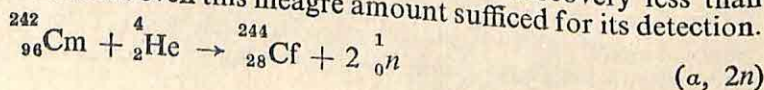
The next two elements, nos. 95 and 96.—americium and curium—were discovered by Ghiorso and Seaborg respectively. Curium was obtained by α -bombardment of plutonium and americium by the β -decay of neutron irradiated plutonium



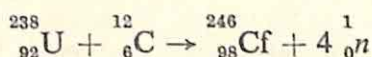
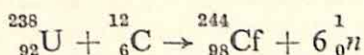
These newly created elements Cm and Am became the target materials for synthesising the next two elements, nos. 97 and 98, berkelium and californium. In 1950, Thompson, Ghiorso and Seaborg bombarded americium with α -particles to produce berkelium :



Continued neutron irradiation of americium gave on β -decay minute quantities of curium. This minute quantity formed the target of intense α -bombardment and led to the formation of californium. At the time of its first discovery less than 5000 atoms could be obtained but even this meagre amount sufficed for its detection.

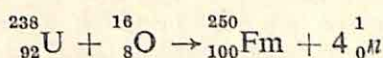
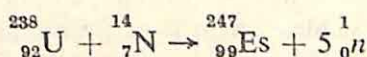


Also by bombarding uranium with carbon nuclei (charge + 6e), Seaborg and his colleagues (1951) obtained two isotopes of californium.

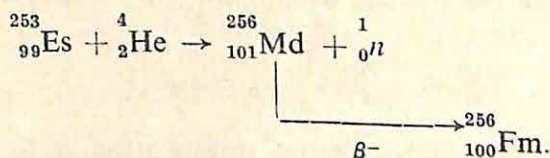


Elements einsteinium and fermium were detected in minute traces during an analysis of the rocks and radioactive fallouts in an island in the Pacific over which an experimental thermonuclear explosion had been carried out in 1952. It is said that the first detection of fermium was made with only 200 atoms of the species. Since then as in the case of other transuranic species, relatively more stable isotopes of these two have been secured by intense neutron bombardment of the preceding members. Successive neutron captures (and β -decay) in nuclear reactors led to the formation of the succeeding members.

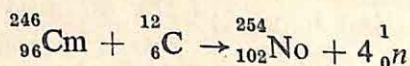
Bombardment of uranium with nitrogen and oxygen nuclei gave einsteinium and fermium respectively



The creation and the subsequent identification of Mendelevium atoms (101) were most difficult. An invisible film of einsteinium electroplated on a gold foil was bombarded with α -particles accelerated in a cyclotron. Mendelevium atoms, which were formed, bounced off and collected on a second gold foil for identification and test. The element Md so produced has a half-life of about 60 min and decays by orbital electron capture to fermium which undergoes immediate fission. It was the fission impulse on the recorder which indicated the death of the mendelevium atoms. In this device, the probability of formation of mendelevium was so low that a single experiment resulted just in the formation of 1 atom of Md on the average. In the original experiments, arrangements were made to herald the news of birth [rather the death which followed immediately on its decay to fermium] of each Md atom by an automatic simultaneous peal of a bell.



The next element nobelium (102) has an element of controversy regarding its first discovery. Its creation was claimed in 1957 by a Swedish laboratory following bombardment of curium-244 target by carbon nuclei (${}^{13}\text{C}$) accelerated in a hilac. This process, repeated in U.S. and U.S.S.R. laboratories, did not yield the element (102). A year later, Ghiorso and others produced the element following the same technique with a different isotope of curium (${}^{246}\text{Cm}$) bombarded by ${}^{12}\text{C}$ ions.



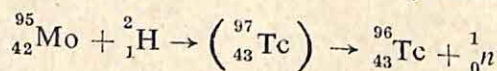
The element no. 103, lawrencium, was produced by the same team in 1961 by bombardment of californium with boron nuclei accelerated in a hilac. All the transuranic elements up to mendelevium have been both physically and chemically identified. The last pair, nobelium and lawrencium, have been detected only by physical tests. All these elements are radioactive, have been detected only by assignment of their atomic numbers and mass numbers with specific activities. The mode of production and the decay characteristics of the products.

XVIII.11. The Actinide Series. The chemical properties of the transuranic elements (nos 93—101) and those of uranium, protoactinium, thorium and actinium exhibit a striking similarity. Starting from Actinium (89) to Lawrencium (103), the atomic number systematically increases but all of them show characteristics of oxidation state (III). All of them therefore acquire the same position in the periodic table like the rare-earth elements, the lanthanides. Thorium however has stable tetravalent compounds. Uranium, neptunium and plutonium have also properties of oxidation state (IV) and (VI).

Indeed there is a close parallelism between the lanthanides and these elements, which are now called "Actinides." Both the lanthanides and actinides, have MX_3 type trihalides; the crystal structures of the trihalides in both these groups are the same. The MX_3 compounds are all isomorphous with one another. The magnetic properties of some similar compounds in the two series are also identical. The lanthanide contraction, *i.e.*, the decrease in size of the ions with increase in atomic number of the rare-earth elements, is also repeated in actinides. Actinides thus illustrate the repetition of lanthanides in the transuranic domain of the periodic table. The synthesis of element (104) and the identification of its characters with those of hafnium would some day establish the truth.

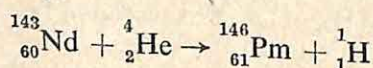
XVIII.12. Gaps in the Periodic Table. There were four vacant places in the periodic table at the beginning of the thirties of the century. These gaps in the table related to elements with atomic nos. 43, 61, 85 and 87. From theoretical considerations of their possible nuclear compositions, all of them were expected to be radioactive and quite unstable. That is why these were not met with in nature. In 1932 neutron was discovered and about that time the different missiles for bombarding nuclei also came to be available. In fact, all these four elements are formed through impingement of their neighbouring elements by suitable high energy projectiles.

Element $Z = 43$, now called technetium (Tc), was produced by bombarding molybdenum ($Z = 42$) with deuterons. It was a (d, n) reaction;



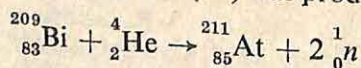
Later on, various other nuclear reactions were used to obtain different isotopes of technetium, all of which were found to be radioactive.

Element with atomic no 61 was originally called illinium. This element was also synthesised by bombardment on neodymium nuclei with α -particles. The reaction is an (α, p) one;

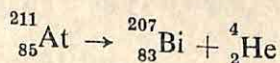


This element ($Z = 61$) has been given the new name of promethium (Pm). This is also radioactive. Several isotopes are known.

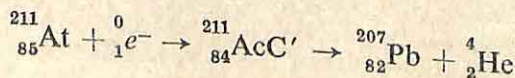
Corson, Mackenzie and Segré bombarded bismuth with α -particles when the element $Z = 85$, now called astatine (At) was produced. This is an ($\alpha, 2n$) reaction;



The astatine obtained is radioactive with a half-life of 7.5 hrs. It yields another isotope of bismuth through α -emission,

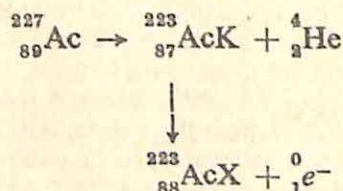


Astatine also undergoes another change through electron capture producing actinium C' , which is a member in the actinium radioactive series. This spontaneously disintegrates into lead.

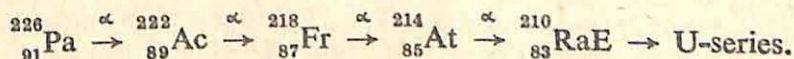


Though astatine exhibits some metallic character, it is a homologue of iodine and have many similarities with the latter.

Element ($Z = 87$) is Francium (Fr). Mlle. M. Perey (1939) discovered this element as one of the products of disintegration in the actinium radioactive series and called it actinium K, which broke down to AcX by β -decay.

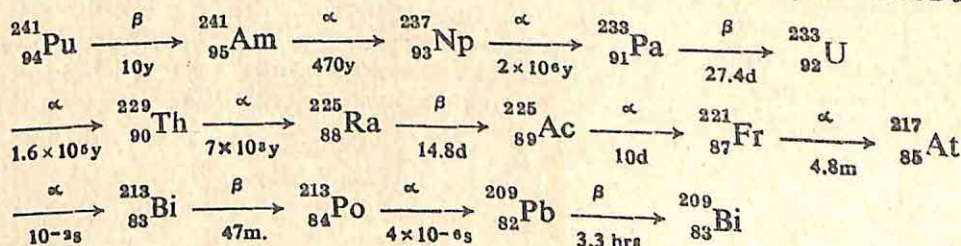


Later on, different nuclear reactions effected artificially also led to the formation of one or other isotope of francium ; e.g.,



The chemical characteristics of francium appear to be similar to those of the alkali-metals, of Gr.I, which is expected from its position in the Table.

XVIII.13. The Neptunium Radioactive Series. The three naturally occurring radioactive series described previously (Chapter V) were long known. These start with uranium, thorium and actinouranium. It was soon observed that all the members of any one of such a series have atomic mass numbers which can be represented by a simple formula. For example, in the thorium series, the mass number of every element may be expressed as $4n$, where n is an integer. For the thorium series, the starting element thorium has a $n = 58$ i.e., mass number = 232, and the series ends in lead, $n = 52$, i.e., mass number, 208. So this series is called $4n$ -series. The uranium series is called $(4n+2)$ -series, every member has a mass number having an n -value between 59 and 51. The parent uranium itself has a mass number $(4 \times 59 + 2) = 238$, and the end is lead, $(4 \times 51 + 2) = 206$. Similarly, the actinium series is the $(4n+3)$ series. The integral values of n varies from 58 to 51. Thus we have $(4n)$, $(4n+2)$, and $(4n+3)$ natural radioactive series ; the missing series is the $(4n+1)$ one. With the discovery of transuranic elements, we come across a new radioactive series. It starts with plutonium (at. no. 94, mass number 241) and ends in bismuth (at no. 83, mass number 209). This has been given the name neptunium radioactive series. It is the $(4n+1)$ series ; for plutonium ($n = 60$) and for bismuth ($n = 52$). The stages in this series may be briefly described as,



XVIII.14. Use of Isotopes. Artificial radioactive isotopes can now be obtained in appreciable amounts and this has increased their applications to such a large extent that even a detailed catalogue of the same is beyond the scope of this text. The outstanding achievement of the study of nuclear reactions and the isotopes elements and (iii) discovery of the elements in the gaps of the periodic table. A few other typical applications will be mentioned here.

The diagnostic and therapeutic uses of isotopes in the field of medicine is now well-known. Radium, for some years now, was often employed in the treatment of cancer. For some of the undesirable effects of its decay products it is now

being slowly replaced by ^{60}Co . The isotope ^{131}I is employed in the treatment of hyperthyroidism. ^{32}P or radiophosphorus is being used in some diseases of the blood by measuring its uptake in the bones.

Tracer Technique. If, in some of the molecules of a substance, one of the constituent atoms of its molecules be of radioisotopic variety, these molecules are said to be labelled or tagged. The proportion of the tagged molecules may be quite small in the whole mass of the substance. The chemical and physiological properties of the normal molecules and those with isotopic constituent are the same. The isotopic variety can be easily and readily detected from its radioactivity with a G-M counter. The element whose radioisotope is introduced is called the "tracer element". By measuring its radioactivity, through the chemical or the physiological process, the fate of the substance at different stages can be discerned. Such a procedure reveals the course, progress and mechanism of a change and it is called 'tracer technique'. The technique is now widely employed and it solves many problems where other methods fail.

The diffusion of lead ions into the solid or liquid may be determined by coating a sample of lead with its isotope radiolead. After a given time, the sample is cut into thin slices and the radioactivity of these slices is measured which gives the extent of diffusion and enables the calculation of the diffusion constant.

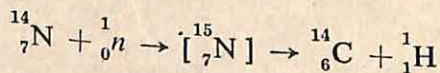
If in a stable phosphatic fertiliser, some amount of the same fertiliser prepared from ^{32}P be added and used. The uptake of phosphates by the plant or its lodging can be easily followed.

Suppose a small amount of acetic acid synthesised with ^{14}C in its methyl group, is added to the stable acetic acid, which is used in physiological system where it yields carbon dioxide. If the collected CO_2 does not show any radioactivity it is obvious that it is the carbonyl group which has participated in the process.

Another instructive example is in the use of isotopes in following the mechanism of photosynthetic process. Plants, in presence of sunlight, may be fed with $^{14}\text{CO}_2$ (and H_2O) along with the stable $^{12}\text{CO}_2$. The formation of the first products of photosynthesis is then followed by measuring the radioactivity at different stages. On the other hand, in some experiments stable CO_2 with H_2^{18}O , (i.e., water with stable isotope of oxygen) was used. The liberated oxygen was tested to find out if the oxygen originated from water. Since non-radioactive isotope is used, mass-spectrometer had to be used for detection.

Batches of rats were fed with diet containing ^{32}P . At different time intervals, bone ash were tested for radioactivity. The results confirmed that a given phosphorus atom remained in the bones for about four weeks and were in eqm. with surroundings. Similarly, sodium chloride solution, tagged with ^{24}Na , injected in blood was followed to find out the rate and directions of circulation. Innumerable other applications are now being made.

Radiocarbon Dating. W. F. Libby suggested that the age of old samples containing carbon could be found out by determining ^{14}C content of the same. In the upper reaches of the atmosphere ^{14}C is being continuously synthesised at a steady rate by the action of neutrons of cosmic rays on stable ^{14}N .



The radio carbon thus formed is converted into carbon dioxide and is ultimately locked in the plants. Animals taking up the plants also contain ^{14}C in their tissues. The amount of ^{14}C present in these systems is about 1×10^{-12} per atom of ordinary carbon. ^{14}C has a half-life of 5568 years. Hence its activity would be 25% after nearly 11000 years.

Suppose now a sample had been first formed t years ago, then its present ^{14}C activity (I_t) is related to its initial activity (I_0) as

$$I_t = I_0 e^{-\lambda t}, \quad \text{where } \lambda = 0.693/5568 \text{ years}^{-1}$$

By measuring the radioactivity of plant samples freshly formed, I_0 is obtained, remembering that the rate of synthesis of ^{14}C is constant. The value is found as

15.3 counts per gm per minute. The present-day radioactivity (I_t) is measured with the sample. It is thus possible to find out t , the age of the sample. In this way samples as old as 25000 years can be dealt with.

Age of the Earth. The earth must be as old as the oldest mineral that can be detected. Applying radioactive methods, the age of some of the minerals could be fixed and found to be several thousand million years. The method is simple. The end products in the disintegration of uranium and thorium minerals is lead. The estimation of lead in such an undisturbed ore today determines the amount of uranium (q_2) which has suffered disintegration since its formation. Further, measurement of the present-day radioactivity of uranium in the ore can also be experimentally determined by analytical methods. Let the amount of uranium present now be q_1 . Then, the original amount of uranium was $(q_1 + q_2)$. From Rutherford's equation,

$$N_t = N_0 e^{-\lambda t}, \quad \text{we have, } q_1 = (q_1 + q_2) e^{-\lambda t}$$

where $\lambda = 0.693/(4.6 \times 10^9)$ years⁻¹.

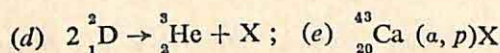
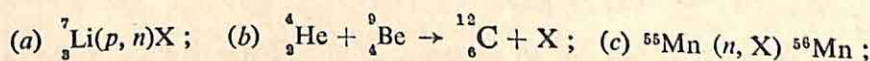
The age of the mineral (t years) is calculated and found to be 4.5×10^9 years. Similar values were also obtained by applying the method to thorium minerals and to rubidium containing minerals, in which ^{87}Rb has a β -decay activity.

References for further reading

- (i) Elementary nuclear theory—Bethe
- (ii) Source book of atomic energy—Glasstone
- (iii) Radioactive isotopes—Whitehouse and Putnam
- (iv) Atomic energy—H. D. Smyth
- (v) Applied radiochemistry—O. Hahn
- (vi) Radioactivity applied to chemistry—Wahl and Bonner.

Problems

1. Solve X in the following :



2. In what time will ${}^{24}\text{Na}$ lose its activity by 80% if its half-life be 15 hours?

3. The half-life of ${}^{14}\text{C}$ is 5600 years. A living sample gives a count of 15.3 counts per gm per min. An old sample is found to give 9.6 counts per gm per min. What is the age of the sample?

4. ${}^{90}\text{Y}$ has a half-life of 64 hours and ${}^{90}\text{Sr}$ 28 years. ${}^{90}\text{Sr}$ decays to ${}^{90}\text{Y}$ by β -emission. What will be the amount of ${}^{90}\text{Y}$ in equilibrium with 1 gm of ${}^{90}\text{Sr}$.

5. In a sample of pitchblende the atomic ratio ${}^{206}\text{Pb} : {}^{238}\text{U} = 0.23 : 1$. Calculate the age of the mineral, if half-life of uranium is taken as 4.5×10^9 years. All lead originated from uranium.

APPENDIX 1.1

UNITS AND DIMENSIONS

The fundamental units chosen are those of *length*, *mass* and *time*. The magnitudes of the units of these three are different in different systems. The most common systems employed are

- (i) C.G.S. system (Centimetre-Gramme-Second system)
- (ii) F.P.S. system (Foot-Pound-Second system)
- (iii) M.K.S. system (Metre-Kilogram-Second system)

The unit of length in the C.G.S. system is the *centimetre*. It is the one-hundredth part of a metre which is the distance between two lines on a bar kept in the exchequer at Paris at 60°C. The *metre* itself is the unit in the M.K.S. system. In the F.P.S. system, the unit of length is the *foot*. It is one third of the distance between two transverse lines on a Pt-Ir bar kept at the Standards Office of the Board of Trade, London, at 62°F. These units are related as

$$1 \text{ cm} = 0.01 \text{ m} = 0.0381 \text{ ft}$$

$$\text{or} \quad 1 \text{ ft} = 30.48 \text{ cms}$$

The unit of mass in the C.G.S.-system is a *gramme* or *gram*. It is the one-thousandth part of a lump of Pt-Ir alloy, called a Kilogram, also kept at the Paris exchequer. It is also equal to mass of water in one c.c. of pure water at 4°C. The Kilogram is the unit of mass in the M.K.S. system. In the F.P.S. system, the unit of mass is the *Pound*, which is the quantity of a Pt-Ir alloy kept as standard in the Standards Office, London. The relation between the different units are,

$$1 \text{ gm} = 0.001 \text{ Kg} = 2.2046 \times 10^{-3} \text{ lb}$$

$$\text{or} \quad 1 \text{ lb} = 453.59 \text{ gm}$$

The *Second* is the unit of time in all systems. It is 1/86400 th part of the *mean solar day*.

All other units used for measuring various physical quantities are derived from these three fundamental units and hence their units are often called derived units. For example, the unit of velocity is a derived unit, as it is expressed in terms of length in unit time. Thus, units of area, volume, pressure, density, work, power, surface-tension, etc., are all derived units.

Dimensions. The fundamental units of mass, length and time are denoted by M, L and T respectively and these are used in obtaining the derived units for other physical quantities. Thus, the area of a surface may be expressed as the product of two lengths, i.e., $\text{area} = L \times L = L^2$. It is said the unit of area is of two dimensions in length. Similarly the volume, $V = L \times L \times L = L^3$, or the unit of volume is of 3 dimensions in length. We can then say, the unit of density

$$= \frac{\text{mass}}{\text{volume}} = \frac{M}{L^3} = M.L^{-3}. \text{ In other words, the unit of density has 1 dimension}$$

in mass and -3 in length. The power to which the fundamental units are to be raised to obtain the derived unit are said to be the dimensions of the latter.

It is also possible to have dimensionless physical entities such as specific gravity, angle, etc., which are all ratios. For example, an angle is a ratio of lengths and hence a number only. When the unit of a physical quantity is expressed in terms of the fundamental units (M, L and T), the relation is called a '*Dimensional Equation*'. Thus, density, $D = M.L^{-3}$. Below is appended a list of such dimensional formulae.

Physical quantity	Dimensions
1. Area = (length) ²	L ²
2. Volume = (length) ³	L ³
3. Velocity = $\frac{\text{Length}}{\text{time}}$	$\frac{L}{T} = LT^{-1}$
4. Acceleration = $\frac{\text{Velocity}}{\text{time}}$	$\frac{LT^{-1}}{T} = LT^{-2}$
5. Density = $\frac{\text{mass}}{\text{volume}}$	$\frac{M}{L^3} = ML^{-3}$
6. Force = mass $\times$ acceleration	$M \times LT^{-2} = MLT^{-2}$
7. Pressure = $\frac{\text{force}}{\text{area}}$	$\frac{MLT^{-2}}{L^2} = ML^{-1}T^{-2}$
8. Momentum = mass $\times$ velocity	$M \times LT^{-1} = MLT^{-1}$
9. Moment of inertia = mass $\times$ (length) ²	ML ²
10. Stress = $\frac{\text{force}}{\text{area}}$	$\frac{MLT^{-2}}{L^2} = ML^{-1}T^{-2}$
11. Strain = $\frac{\text{change of length}}{\text{original length}}$	no dimension
12. Coefficient of elasticity = $\frac{\text{stress}}{\text{strain}}$	ML ⁻¹ T ⁻²
13. Surface tension = $\frac{\text{force}}{\text{length}}$	$\frac{MLT^{-2}}{L} = MT^{-2}$
14. Work = force $\times$ distance	MLT ⁻² $\times$ L = ML ² T ⁻²
15. Potential energy = mass $\times$ acc. $\times$ distance	M $\times$ LT ⁻² $\times$ L = ML ² T ⁻²
16. Kinetic energy = $\frac{1}{2}$ mass $\times$ (velocity) ²	M $\times$ (LT ⁻¹) ² = ML ² T ⁻²
17. Power = $\frac{\text{work}}{\text{time}}$	$\frac{ML^2T^{-2}}{T} = ML^2T^{-3}$
18. Coefficient of viscosity = stress per unit velocity gradient = $\frac{\text{force/area}}{\text{velocity/distance}}$	$\frac{MLT^{-2}/L^2}{LT^{-1}/L} = ML^{-1}T^{-1}$

For the quantities in electricity and magnetism, a fourth fundamental unit has to be defined. In the C.G.S. system, the dielectric constant, ϵ , or the permeability, μ , has been accepted as fundamental. In electrostatics, the force between

point electric charges is given by $F = \frac{Q_1 Q_2}{\epsilon d^2}$, where ϵ is the dielectric constant of the medium.

The dielectric constant, ϵ_0 , of the free space (vacuo) in e.s.u. is taken as unity and dimensionless. So, the unit charge becomes the charge which repels a similar charge 1 cm away with a force of 1 dyne.

$$\therefore F = \frac{Q^2}{\epsilon_0 d^2}$$

or, dimensionally

$$(MLT^{-2}) = \left[\frac{Q^2}{\epsilon_0 L^2} \right]$$

Hence, the dimensions of the electric charge, $[Q] = \epsilon_0^{\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}$

In the same way, in electromagnetism, the force between two magnetic poles is given by

$$F = \frac{m_1 m_2}{\mu d^2} \text{ where } \mu \text{ is the magnetic permeability of the medium,}$$

In e.m.u., the permeability in free space, μ_0 is taken as unity and is regarded dimensionless. Therefore, the pole which repels an identical pole 1 cm away with a force of 1 dyne in vacuo is the unit pole. Then

$$F = \frac{m^2}{\mu_0 d^2} \quad \text{or} \quad [MLT^{-2}] = \left[\frac{m^2}{\mu_0 d^2} \right]$$

Hence the dimension of the pole strength, $[m] = \mu_0^{\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}$

The magnetic field strength, H , is given by $F = H.m$.

$$\text{or} \quad H = \frac{F}{m} = \frac{MLT^{-2}}{\mu_0^{\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}} = \mu_0^{-\frac{1}{2}} M^{\frac{1}{2}} L^{-\frac{1}{2}} T^{-1}$$

Physical quantity	Electrostatic system		Electromagnetic system	
	Relation	Dimension	Relation	Dimension
1. Quantity of electricity	$Q = F\epsilon d^2$	$\epsilon_0^{\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}$	$Q = IT$	$[\mu_0^{-\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}] [T]$ $= \mu_0^{-\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{1}{2}}$
2. Current	$I = Q/T$	$\epsilon_0^{\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}$	$I = \frac{Hr}{2\pi m}$	$[\mu_0^{-\frac{1}{2}} M^{\frac{1}{2}} L^{-\frac{1}{2}} T^{-1}] [L]$ $= \mu_0^{-\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}$
3. Potential	$V = W/Q$	$\epsilon_0^{-\frac{1}{2}} L^{\frac{1}{2}} M^{\frac{1}{2}} T^{-1}$	$V = W/Q$	$[ML^2 T^{-2} / \mu_0^{-\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{1}{2}}]$ $= \mu_0^{\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}$
4. Resistance	$R = V/I$	$L^{-1} T \epsilon_0^{-1}$	$R = V/I$	$[\mu_0^{\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2} / \mu_0^{-\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{1}{2}}]$ $T^{-1}] = \mu_0 LT^{-1}$
5. Electrical Energy,	$E = VIT$	$ML^2 T^{-2}$	$E = VQ$	$ML^2 T^{-2}$
6. Electric Power	$P = E/T$	$ML^2 T^{-3}$	$P = \frac{W}{T}$	$ML^2 T^{-3}$

To compare the electrostatic and electromagnetic systems of units, it would be necessary to find out a relation between ϵ_0 and μ_0 . If we take the dimensions of the quantity of electricity in the two systems, we have, $\mu_0^{-\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{1}{2}} = \epsilon_0^{\frac{1}{2}} M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}$

$$\text{or} \quad \left[\frac{1}{\mu_0 \epsilon_0} \right]^{\frac{1}{2}} = LT^{-1}$$

which is the dimension of velocity. By comparing the magnitudes of a physical quantity in the two systems, the actual value is found to be 3×10^{10} , or c , the velocity of light, i.e.,

$$\frac{1}{\mu_0 \epsilon_0} = c^2$$

APPENDIX I.2

The pressure exerted by a gas. Let us take a quantity of gas occupying a volume v c.c. and containing N molecules. The number of molecules per c.c., $n = \frac{N}{v}$.

Suppose out of these n molecules per c.c., there are

n_1 molecules each having a velocity c_1 ,

n_2 molecules each having a velocity c_2 ,

n_3 molecules each having a velocity c_3 , and so on.

Then we have, $n = n_1 + n_2 + n_3 + \dots$

$$\text{and } \bar{c}^2 = \frac{1}{n} (n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \dots) = \frac{\sum n_i c_i^2}{n} \dots (A)$$

where c is the root-mean-square velocity.

Again suppose out of the n_1 molecules (each having a velocity c_1)

n' molecules have each a velocity component x' along x -axis,

n'' molecules have each a velocity component x'' along x -axis, and so on.

Then, $n_1 = n' + n'' + n''' + \dots$

$$\text{and } \bar{x}^2 = \frac{1}{n_1} (n' x'^2 + n'' x''^2 + n''' x'''^2 + \dots) = \frac{\sum n' x'^2}{n_1} \dots (B)$$

$$\text{and also } \bar{x}^2 = \frac{1}{3} c_1^2$$

Now consider a unit area of the wall at rt-angles to the direction of the x -axis. Let us attempt to find out the impact of the molecules on this area.

First consider the group of molecules which have a component velocity x' along this axis. In one second, all such molecules which are at a distance x' from the wall will strike the surface. These molecules are therefore present in the volume $(x' \times 1) = x'$ c.c. Since there are n' such molecules per c.c. the total number of molecules in x' c.c. is $n'x'$. Again, because both the directions along x -axis are equally possible, the number of molecules which will strike the surface is $\frac{1}{2}n'x'$. In each collision, the momentum of the molecule before impact is mx' and after the perfectly elastic collision, the momentum would be $-mx'$. Therefore, the change of momentum = $2mx'$. The net-change of momentum for all the molecules of this group (having x' component) is $2mx' \times \frac{1}{2}n'x' = mn'x'^2$.

If we now consider the change of momentum of other molecules having x -axis components x'' , x''' etc., we have the change of momentum per sec

$$= mn'x'^2 + mn''x''^2 + mn'''x'''^2 + \dots$$

$$= m \sum n' x'^2 = mn_1 \bar{x}^2$$

$$= \frac{1}{3} mn_1 c_1^2$$

... from (B)

Next, we should consider all the molecules having all possible velocities, c_1, c_2, c_3 etc. The change of momentum resulting from the impacts of all such molecules, would be,

$$= \frac{1}{3} mn_1 c_1^2 + \frac{1}{3} mn_2 c_2^2 + \frac{1}{3} mn_3 c_3^2 + \dots$$

$$= \frac{1}{3} m \sum n_i c_i^2 = \frac{1}{3} mnc^2$$

... (from A)

$$= \frac{1}{3} m \frac{N}{v} \bar{c}^2$$

But the change of momentum per unit area per unit time is the force acting on unit area i.e., the pressure, P .

$$\therefore P = \frac{1}{3} m \frac{N}{v} \bar{c}^2 \quad \text{or} \quad Pv = \frac{1}{3} mN\bar{c}^2$$

APPENDIX I.3

Integrals of the type $\int_0^\infty e^{-ax^2} x^n dx$ occur very often in problems of physical chemistry. The results of such integrals are tabled here.

$$(i) \int_0^\infty e^{-ax^2} x dx$$

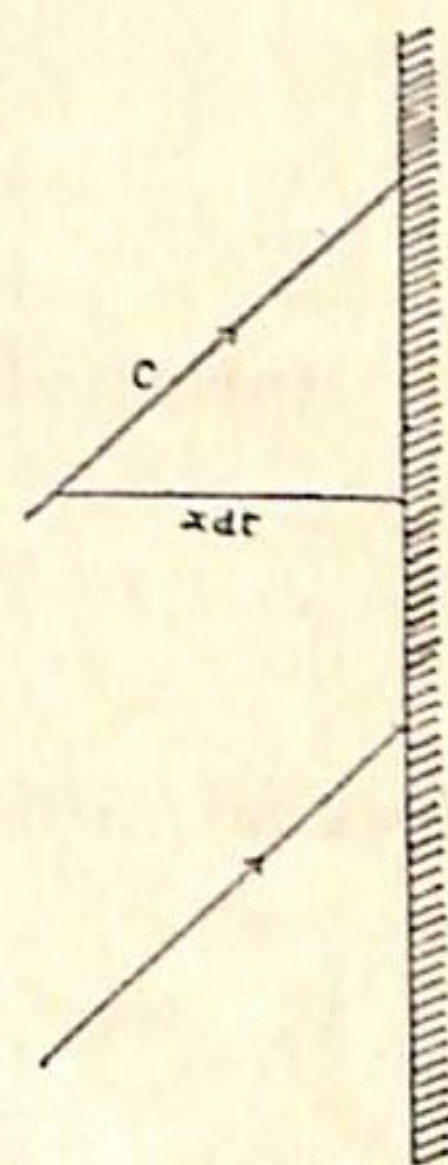


FIG. AI.2

Let $x^2 = z$, then $\int_0^\infty e^{-ax^2} x dx = \frac{1}{2} \int_0^\infty e^{-az} dz = \frac{1}{2} \left[\frac{e^{-az}}{-a} \right]_0^\infty = \frac{1}{2a}$

(ii) $\int_0^\infty e^{-ax^2} x^3 dx = -\frac{d}{da} \int_0^\infty e^{-ax^2} x dx = \frac{1}{2a^2}$

(iii) $\int_0^\infty e^{-ax^2} dx$

Let us start with the following : $\int_0^\infty \int_0^\infty e^{-a(x^2+y^2)} dx dy$.

Put $x^2+y^2 = r^2$. Then $r dr d\theta = dx dy$

$$\begin{aligned} \therefore \int_0^\infty \int_0^\infty e^{-a(x^2+y^2)} dx dy &= \int_0^{\pi/2} \int_0^\infty e^{-ar^2} r d\theta dr = \pi/2 \int_0^\infty e^{-ar^2} r dr \\ &= \pi/2 \int_0^\infty e^{-az} dz = \frac{\pi}{2} \cdot \frac{1}{2a}, \end{aligned}$$

substituting $z = r^2$, and thus $dz = 2r dr$.

$$\therefore \int_0^\infty \int_0^\infty e^{-a(x^2+y^2)} dx dy = \frac{\pi}{4a}$$

Since all values for x and y are permissible, so let $x = y$, then,

$$\int_0^\infty \int_0^\infty e^{-a(x^2+y^2)} dx dy = \left[\int_0^\infty e^{-ax^2} dx \right]^2 = \frac{\pi}{4a} \text{ or } \int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

TABLE OF INTEGRALS $f(x) = \int_0^\infty x^n e^{-ax^2} dx$

n	$f(x)$	n	$f(x)$
0	$\frac{1}{2} \sqrt{\frac{\pi}{a}}$	1	$\frac{1}{2a}$
2	$\frac{1}{4} \sqrt{\frac{\pi}{a^3}}$	3	$\frac{1}{2a^2}$
4	$\frac{3}{8} \sqrt{\frac{\pi}{a^5}}$	5	$\frac{1}{a^3}$

Some useful expansions : When x^2 is less than unity,

$$(1+x)^{-1} = 1 - x + x^2 - x^3 + \dots$$

$$(1-x)^{-1} = 1 + x + x^2 + x^3 + \dots$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

$$\ln(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4} \dots$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots$$

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots$$

APPENDIX II

SOME IMPORTANT PHYSICAL CONSTANTS

<i>Physical quantity</i>	<i>Magnitudes</i>
Electronic charge (e)	4.8028×10^{-10} esu
Avogadro constant (N_0)	6.0247×10^{23} molecules/mole
Boltzmann constant (k)	1.3804×10^{-16} ergs/deg
Faraday constant (F)	96493 Coulombs/equivalent
Velocity of light (c)	2.9979×10^{10} cms/sec
Planck constant (h)	6.6252×10^{-27} ergs-sec
The gas constant (R)	8.316×10^7 ergs/deg/mole
Rest mass of electron (m_e)	9.109×10^{-28} gm
Rest mass of proton (m_H)	1.673×10^{-24} gm
Ratio, m_H/m_e	1.837×10^3

Conversion factors

1 atmosphere	= 1,013,250 dynes/cm ²
1 calorie	= 4.1840 joules
1 electron volt	= 1.602×10^{-12} egrs
1 amu	= 931.16 Mev
1 gm	= 5.6099×10^{26} Mev
1 Mev	= 1.07×10^{-3} mass unit
	= 1.6×10^{-8} ergs = 4.45×10^{-20} KWH

APPENDIX III

THE B.E.T. EQUATION (See Sec. XV.5)

According to this theory, the adsorbed layer may be multimolecular thick and there is dynamic equilibrium between the successive layers. It is further assumed that the heat of adsorption in each layer excepting the first one is the same as the latent heat of condensation, L . The energy of activation for desorption of molecules from the first layer is E (say). At a temperature T and pressure p , let

- θ_0 = fraction of the surface empty
 θ_1 = fraction of the surface covered with a single layer
 θ_2 = fraction of the surface covered with a second layer
 θ_i = fraction of the surface covered with i -th layer.

Further let x_m be the number of molecules adsorbed per cm^2 in a completed layer. Now considering at eqm, the rate of adsorption equal to that of desorption at the first layer, we have

$$kp\theta_0 = x_m\theta_1\nu_1e^{-E/RT} \quad \dots (1)$$

where ν_1 is the frequency of oscillation of the adsorbed molecules. For the equilibria in successive layers, we can write

$$kp\theta_1 = x_m\theta_2\nu e^{-L/RT} \quad \dots (2)$$

$$kp\theta_2 = x_m\theta_3\nu e^{-L/RT} \quad \dots (3)$$

$$kp\theta_{i-1} = x_m\theta_i\nu e^{-L/RT} \text{ etc.} \quad \dots (4)$$

remembering that the frequency of oscillation ν would be the same for all layers excepting the first.

$$\text{From (1), } \theta_1/\theta_0 = \frac{kpe^{E/RT}}{x_m\nu_1} = \alpha \text{ (say)} \quad \dots (5)$$

$$\text{or } \theta_1 = \alpha\theta_0 \quad \dots (6)$$

$$\text{from (2) } \theta_2/\theta_1 = \frac{kpe^{L/RT}}{x_m\nu} = \beta \text{ (say)} \quad \dots (7)$$

$$\text{or } \theta_2 = \beta\theta_1 = \alpha\beta\theta_0 = \gamma\beta^2\theta_0 \quad \dots (8)$$

$$\text{putting } \alpha/\beta = \gamma \quad \dots (9)$$

$$\text{Similarly, } \theta_3/\theta_2 = \beta, \text{ or } \theta_3 = \beta\theta_2 = \gamma\beta^3\theta_0 \quad \dots (10)$$

$$\text{and hence } \theta_i = \gamma\beta^i\theta_0 \quad \dots (11)$$

$$\text{Obviously, } \gamma = \alpha/\beta = \frac{\nu}{\nu_1} e^{(E-L)/RT}, \text{ by (5) and (7)} \quad \dots (12)$$

Now, the total adsorption per sq. cm of the surface,

$$\begin{aligned} x &= x_m [\theta_1 + 2\theta_2 + 3\theta_3 + \dots + i\theta_i + \dots] \\ (\because \alpha\theta_0 &= \gamma\beta\theta_0) \quad = x_m [\gamma\beta\theta_0 + 2\gamma\beta^2\theta_0 + 3\gamma\beta^3\theta_0 + \dots + i\gamma\beta^i\theta_0 + \dots] \\ &= x_m\gamma\theta_0 \left[\sum i\beta^i \right]_{i=1}^{\infty} = x_m\gamma\theta_0 \frac{\beta}{(1-\beta)^2} \quad \dots (13) \end{aligned}$$

$$\text{Hence } x/x_m = \gamma\theta_0 \frac{\beta}{(1-\beta)^2} \quad \dots (14a)$$

Expressing adsorbates in term of volumes $\frac{v}{v_m} = \frac{x}{x_m}$,

We have
$$v/v_m = \gamma \theta_0 \frac{\beta}{(1-\beta)^2} \quad \dots (14)$$

The evaluation of θ_0 may be made as follows :

$$\begin{aligned} \theta_0 &= 1 - (\theta_1 + \theta_2 + \theta_3 + \dots \theta_t + \dots) \\ &= 1 - (\gamma\beta\theta_0 + \gamma\beta^2\theta_0 + \gamma\beta^3\theta_0 + \dots) \\ &= 1 - \gamma\theta_0 \left[\sum_{l=1}^{\infty} \beta^l \right] = 1 - \gamma\theta_0 \frac{\beta}{1-\beta} \end{aligned}$$

or
$$\theta_0 = \frac{1}{1 + \frac{\gamma\beta}{1-\beta}} \quad \dots (15)$$

Substituting (15) in (14),

$$v/v_m = \frac{\gamma\beta}{(1-\beta)^2 \left[1 + \frac{\gamma\beta}{1-\beta} \right]} = \frac{\gamma\beta}{(1-\beta)(1-\beta+\gamma\beta)} \quad \dots (16)$$

If the eqm pressure is made equal to the saturated vapour pressure (p_0) of the adsorbate, then x , amount of molecules adsorbed would be infinitely large and from (14a), $\beta = 1$.

That is,
$$\frac{kp_0 e^{L/RT}}{x_m v} = \beta = 1$$

Comparing this with (7), $\beta = p/p_0 \quad \dots (17)$

The equation (16) then reduces to
$$v/v_m = \frac{\gamma(p/p_0)}{(1-p/p_0)[1+(\gamma-1)p/p_0]}$$

which may be rewritten as,
$$\frac{p}{v(p_0-p)} = \frac{1}{v_m \gamma} + \frac{\gamma-1}{v_m \gamma} \cdot \frac{p}{p_0} \quad \dots (18)$$

which is the B-E-T relation.

CLAUSIUS MOSOTTI RELATION

A simple, though somewhat approximate, derivation of this relation may be made as follows : Consider a substance of mol wt. M , density d and dielectric constant D present between two plates of a condenser with charges $+Q$ and $-Q$. The field of force due to the charges be F which act on the molecules of the substance so as to produce an average induced moment $\bar{m}$ per molecule. Let Z be the induced moment per c.c.

Then, the number of molecules per c.c. $= \frac{N.d}{M}$, where N = Avogadro number.

$$\therefore \text{the moment induced per c.c., } Z = \bar{m} \cdot \frac{N.d}{M} \quad \dots (i)$$

Now take a thin slice of the dielectric between the plates having thickness x , cross-section a , i.e., volume ax . Then induced moment is axZ .

But the induced moment = charge $\times$ distance (x)

$$\text{i.e., charge, (on the surface of the slice)} = \pm \frac{a.x.Z}{x} = \pm aZ$$

$$\text{or, charge density} = \pm Z$$

If the slice were inclined at an angle θ to the direction of the field, then the charge density would be $\pm Z \sin \theta$.

If the slice of the material be now imagined to increase in size as to be large enough just to fill up the entire space between the plates, Fig. (A.IV.1), we have the charge on the plates $= \pm Q$ and the charge on the surface of the dielectric adjoining the plates $= \pm Z$

Hence the effective charge $= Q - Z$.

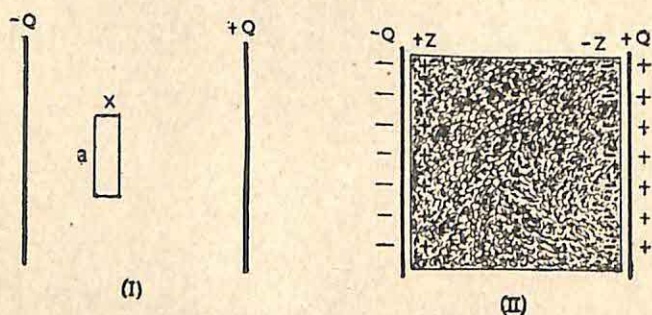


Fig. A.IV.1

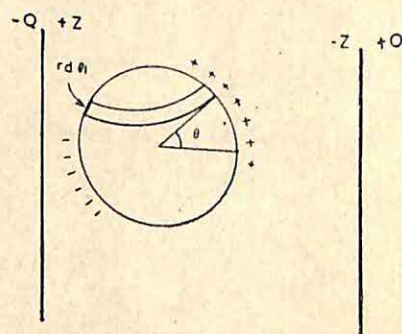


Fig. A.IV.2

By definition, we have, dielectric constant, $D = \frac{Q}{Q-Z}$

Now let us find out the field strength i.e., the force exerted on a unit positive charge inside the dielectric. The unit charge is subject to two forces :

(i) the force (F_1) due to the charge ($Q-Z$) on the plate-medium interface and (ii) the force (F_2) exerted by the layers of molecules surrounding it. This latter force may be calculated by considering the unit charge in a cavity enclosed in a sphere of induced charges. The net force, $F = F_1 + F_2$.

To determine the magnitude of F_2 , we may imagine the surface of the surrounding sphere divided into strips. Imagine a strip on the sphere between angles θ and $\theta + d\theta$ (Fig. A.IV.2) The area of the strip $= 2\pi r \cos \theta \times r d\theta$.

The strip makes an angle θ to the field, then the charge density $= Z \sin \theta$
 $\therefore$ the total charge on the strip $= 2\pi r^2 Z \cos \theta \cdot \sin \theta d\theta$

Hence the force on unit charge $= \frac{1}{r^2} 2\pi r^2 Z \cos \theta \sin \theta d\theta = 2\pi Z \cos \theta \sin \theta d\theta$.

The force exerted on unit charge parallel to the field $= 2\pi Z \sin \theta \cos \theta d\theta \times \sin \theta$

To evaluate the total force exerted by the entire surface of the sphere, we may integrate the above for 0 to $\pi/2$ and double the same, i.e.,

$$F_2 = 2 \times \int_0^{\pi/2} 2\pi Z \sin^2 \theta \cos \theta d\theta = 4\pi Z \left[\frac{\sin^3 \theta}{3} \right]_0^{\pi/2} = \frac{4\pi Z}{3}.$$

The force F_1 , due to plate-charge is given by $F_1 = 4\pi (Q-Z)$.

$$\therefore F = 4\pi (Q-Z) + \frac{4\pi Z}{3}$$

or

$$3F = 12\pi Q - 8\pi Z$$

i.e.,

$$12\pi Q = 3F + 8\pi Z$$

and

$$12\pi Q - 12\pi Z = 3F - 4\pi Z.$$

$$\therefore D = \frac{Q}{Q-Z} = \frac{3F+8\pi Z}{3F-4\pi Z}.$$

So that

$$\frac{D-1}{D+2} = \frac{12\pi Z}{9F} = \frac{4\pi}{3} \cdot \frac{Z}{F}$$

$$= \frac{4\pi}{3} \cdot \frac{N \cdot d}{M} \cdot \bar{m} \cdot \frac{1}{F} \text{ [substituting from (i)]}$$

But $\bar{m} = \alpha F$, where α is the polarisability of the molecule.

$$\therefore \frac{D-1}{D+2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \alpha$$

$\left[\frac{D-1}{D+2} \cdot \frac{M}{d} \right]$ is the molar polarisation, P_t .

$$\text{Hence} \quad P_t = \frac{4\pi N}{3} \alpha.$$

This is Clausius Mosotti relation.

APPENDIX V

ORIENTATION POLARISATION : DEBYE EQUATION

The orientation polarisation comes into the picture only when the molecules are polar. In the absence of any field the dipoles will be lined up in all directions and would not contribute to polarisability of the dielectric. When a field is applied, the dipoles would tend to line up with the field.

The electrostatic energy ϵ of a polar molecule for an orientation θ with the direction of the applied field F is, $\epsilon = -F\mu \cos \theta$, where μ is the moment of the molecule.

Applying Boltzmann-Maxwell statistics, we can find out the average value of this energy for all the molecules,

$$\bar{\epsilon} = \frac{\int_{-\infty}^{+\infty} e^{-\epsilon/kT} \epsilon \, dx \dots dy}{\int_{-\infty}^{+\infty} e^{-\epsilon/kT} \, dx \dots dy} = \frac{\int_{-\infty}^{+\infty} e^{F\mu \cos \theta / kT} \cdot (-F\mu \cos \theta) \, d(-F\mu \cos \theta)}{\int_{-\infty}^{+\infty} e^{F\mu \cos \theta / kT} \cdot d(-F\mu \cos \theta)}$$

Putting $a = \frac{F\mu}{kT}$ and $x = \cos \theta$,

$$\begin{aligned} \bar{\epsilon} &= (-F\mu) \frac{\int_{-1}^{+1} e^{ax} \cdot x \, dx}{\int_{-1}^{+1} e^{ax} \, dx} = (-F\mu) \cdot \frac{\left[\frac{1}{a} e^{ax} \cdot x - \frac{1}{a^2} e^{ax} \right]_{-1}^{+1}}{\left[\frac{1}{a} e^{ax} \right]_{-1}^{+1}} \\ &= - (F\mu) \frac{e^a - \frac{1}{a} e^a + e^{-a} + \frac{1}{a} e^{-a}}{e^a - e^{-a}} = (-F\mu) \left[\frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \right] \\ &= -F\mu \left[\coth a - \frac{1}{a} \right] \approx -F\mu \frac{a}{3}. \end{aligned}$$

$$\text{i.e.,} \quad \bar{\epsilon} = -F\mu \frac{a}{3} = -F\mu \cdot \frac{F\mu}{3kT} = -\frac{\mu^2}{3kT} F^2$$

If the average moment acquired due to orientation be $\bar{\mu}_0$, then $\bar{\epsilon} = -F\bar{\mu}_0$

$$\text{or} \quad \bar{\mu}_0 = -\frac{\mu^2}{3kT} F.$$

But $\bar{\mu}_0 = \alpha_0 F$, where μ_0 is the orientation polarisability

$$\therefore \quad \alpha_0 = -\frac{\mu^2}{3kT}.$$

The total polarisation $P_t = \frac{D-1}{D+2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \alpha$, where α is the net polarisability, both due to distortion as also orientation, Hence,

$$P_t = \frac{4\pi N}{3} \left[\alpha_d + \alpha_e + \alpha_0 \right] = \frac{4\pi N}{3} \left[\alpha_d + \frac{\mu^2}{3kT} \right]$$

This is Debye equation.

DETERMINATION OF AVOGADRO'S NUMBER

In chapter XVI, two methods for the determination of Avogadro's number (N_0) from Brownian motion of sol particles, have been described. A number of other methods, based on distinctly different phenomena, have also been employed. A few of these methods are briefly enumerated below :

(i) *From electric charge, e .* The charge carried by a gm-ion of hydrogen has been found to be 96489 coulombs.

Therefore $N_0 \cdot e = 96489 \times 2.997 \times 10^9$ e.s. units

A knowledge of electronic charge (e) from direct measurement thus gives a value of N_0 . The value of e has been obtained by different methods, such as from Millikan's oil drop in electric field, from radioactive decay, from charge on α -particle, from X'-ray methods, etc. If we accept Millikan's value of e as 4.77×10^{-10} e.s.u., then

$$N_0 = \frac{96489 \times 2.997 \times 10^9}{4.77 \times 10^{-10}} = 6.06 \times 10^{23}$$

(ii) *From Kinetic theory.* We have seen, the mean free path (l) of a gas is given by

$$l = \frac{1}{\sqrt{2}\pi\sigma^2n}, \quad \dots (A)$$

where n = no of molecules present per c.c. (Loschmidt's number) and σ = diameter of the molecule. Now if v denotes the net volume of all the molecules present in 1 c.c. of the gas, then

$$v = \frac{\pi}{6} \sigma^3 n. \quad \dots (B)$$

From (A) and (B), we have $v^2 l^3 = \frac{1}{72\sqrt{2}\pi n}$, i.e., $n = \frac{1}{72\sqrt{2}\pi v^2 l^3}$

$$\therefore N_0 = \frac{22400}{72\sqrt{2}\pi v^2 l^3}$$

The value of l is obtained from viscosity measurement using the relation $\mu = \frac{1}{3}\rho\bar{c}l$, where $\bar{c}$ is the average velocity of the molecules and ρ , the density of the gas.

The value of v is often taken from van der Waals ' b ', i.e., $v = b/4$. Sometimes refractive index value is used to obtain v , from the relation $v = \frac{\mu^2 - 1}{\mu^2 + 2}$

(iii) *From radioactivity.* Each α -particle ejected from a radioactive source ultimately turns into a helium atom. The number of α -particles produced per second and the volume of helium gas resulting therefrom were directly measured. The number of helium atoms (i.e., molecules) per c.c. (n) was thus known.

When 1 gm of radium is in equilibrium with its products, the number of α -particles produced per second is 4 times the quantity (z) ejected per sec from 1 gm of radium alone. Rutherford and his coworkers showed that $z = 3.7 \times 10^{10}$ from different types of experiments on the disintegration of radium.

On the other hand, it was also found by them that 156 c.mm. of helium gas was produced per year from 1 gm of radium in equilibrium with its products. Hence

$$4z \times (365 \times 24 \times 60 \times 60) = 156 \times 10^{-3} \times n$$

i.e.,
$$n = \frac{4 \times 3.7 \times 10^{10} \times 365 \times 24 \times 60 \times 60}{156 \times 10^{-3}} = 2.96 \times 10^{19}$$

whence
$$N_0 = 22400 \times 2.96 \times 10^{19} = 6.6 \times 10^{23}$$

Curie and Dibiérne repeated the method with polonium and found $N_0 = 6.5 \times 10^{23}$

(iv) *From intensity of light.* Planck's equation for the intensity of isothermal radiation (I_λ) at temp. T is given by

$$I_\lambda = \frac{2\pi c^2 h}{\lambda^5} \cdot \frac{1}{e^{N_0 c h / RT\lambda} - 1} = \frac{2\pi c^2 h}{\lambda^5} \cdot \frac{1}{e^{N_0 c h / RT\lambda} - 1}$$

[h = Planck's constant, c = velocity of light.]

Calculations from measurements of I_λ gives the value of $N_0 = 6.2 \times 10^{23}$.

In another method, the intensity of light (I) diffused by a cubic centimetre of liquid due to fluctuations of density is given by

$$I = \frac{\pi^2 RT (\mu^2 - 1)^2 (\mu^2 + 2)^2}{18 N_0 \lambda^4 \left(-v_0 \frac{\partial p}{\partial v_0} \right)}$$

where v_0 = specific volume and $\frac{\partial p}{\partial v_0}$ = isothermal compressibility. The value of N_0 obtained from this relation is 7.5×10^{23} .

(v) *From diffusion experiments.* The equation (VII.a) in section 16.9, shows that if D be the coefficient of diffusion of spherical molecules or particles, we have

$$N_0 = \frac{RT}{D} \cdot \frac{1}{6\pi\eta r}$$

Using experimental values of ' D ' and obtaining r from viscosity measurements of sugar solutions, N_0 was evaluated and found to be 6.5×10^{23} (Einstein).

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